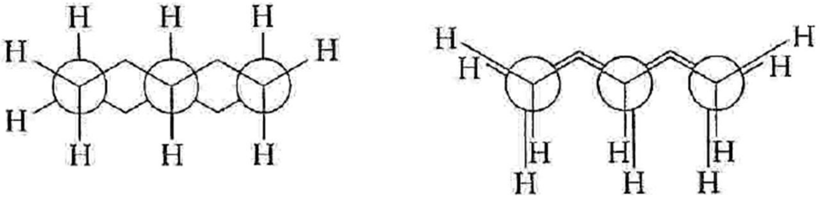
***4.47** Newman izdüşümlerini kullanarak *cis-* ve *trans-* dekalinin köprü başı atomlarındaki sübstitüentlerin bağıl konumlarını çiziniz. Bu izomerlerden hangisinin daha kararlı olmasını beklersiniz, niçin?

*4.47



trans *cis*

The *trans* isomer would be more stable because it can have both of its rings in the favored chair conformation, avoiding the many eclipsing interactions found in the doubly boat conformation of the *cis* isomer (which would actually increase its stability slightly by twisting to avoid some eclipsing interactions).

***4.48** En fazla dört karbonlu herhangi iki bileşikten çıkarak dodekan, $CH_3(CH_2)_{10}CH_3$, sentezi için eşitlikleri yazınız.

*4.48 $H{-}C{\equiv}C{-}C{\equiv}C{-}H \xrightarrow[\text{2 mol equiv. } CH_3(CH_2)_3Br]{\text{2 mol equiv. } LiNH_2}$

$$CH_3(CH_2)_3{-}C{\equiv}C{-}C{\equiv}C{-}(CH_2)_3CH_3 \xrightarrow[\text{Pt catalyst}]{H_2} CH_3(CH_2)_{10}CH_3$$

Stereokimya: Kiral Moleküller

Problem 5.1

Aşağıdaki nesnelerin her birini kiral veya akiral oluşlarına göre sınıflandırınız.

(a) Tornavida
(b) Beyzbol sopası
(c) Golf sopası
(d) Tenis ayakkabısı
(e) Kulak
(f) Odun vidası
(g) Otomobil
(h) Çekiç

5.1 (a) Achiral (b) Achiral
(c) Chiral (d) Chiral
(e) Chiral (f) Chiral
(g) Chiral (h) Achiral

Problem 5.2

Eğer modelleriniz varsa, Şekil 5.3'te gösterilen 2-bütanol modellerini kurunuz ve gerçekten çakışmaz olduklarını kendiniz görünüz. (a) Benzer modelleri 2-bromopropan için kurunuz. Onlar çakışıyorlar mı? (b) 2-Bromopropan molekülü kiral midir? (c) 2-Bromopropanın enantiyomerik yapılarını bulmayı umuyor musunuz?

5.2 (a) Yes (b) No (c) No

Modeller oluşturarak Şekil 5.5'te gösterdiğimizin geçerliliğini gösteriniz. **III** ve **IV**'ün, bir nesne ile onun ayna görüntüsü ilişkisinde olduğunu ve *çakışmadıklarını* (yani **III** ve **IV**'ün kiral moleküller ve enantiyomerler olduklarını) kendi kendinize gösteriniz. (a) Şimdi **IV**'ü alınız ve herhangi iki grubun yerlerini değiştiriniz. Moleküller arasındaki yeni ilişki nedir? (b) Şimdi, her iki modeli alınız ve herhangi iki grubun yerini değiştiriniz. Moleküller arasındaki ilişki şimdi nedir?

Problem 5.3

Kimyanın üç boyu
işin içine girdiğinc

5.3 (a) They are the same molecule. (b) They are enantiomers.

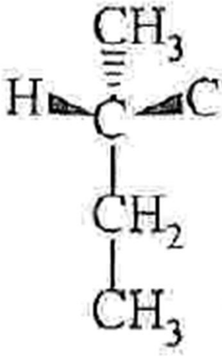
Burada listelenmiş moleküllerin bazıları bir stereomerkeze sahiptir, bazıları sahip değildir. Stereomerkeze sahip olan moleküllerin her iki enantiyomeri için üç boyutlu formülleri yazınız.

Problem 5.4

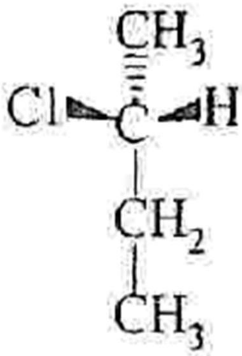
(a) 2-Floropropan	**(e)** 2-Bromopentan
(b) 2-Metilbütan	**(f)** 3- Metilpentan
(c) 2-Klorobütan	**(g)** 3-Metilheksan
(d) 2-Metil-1-bütanol	**(h)** 1-Kloro-2-metilbütan

5.4 (a), (b), and (f) do not have stereocenters.

(c)

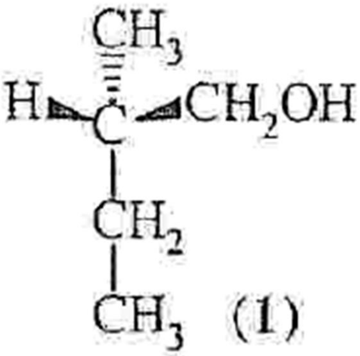


(1)

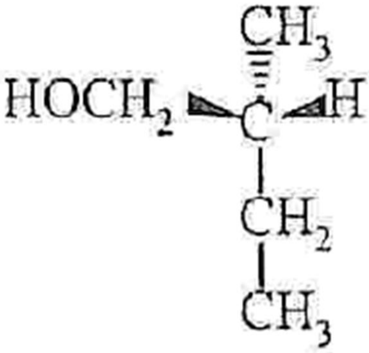


(2)

(d)

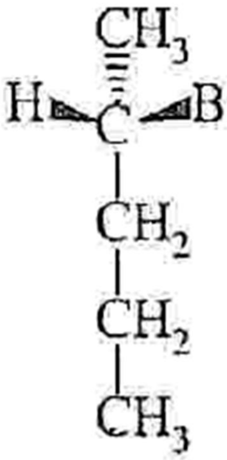


(1)

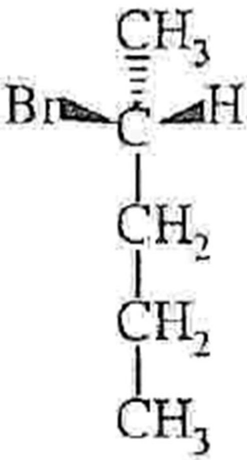


(2)

(e)

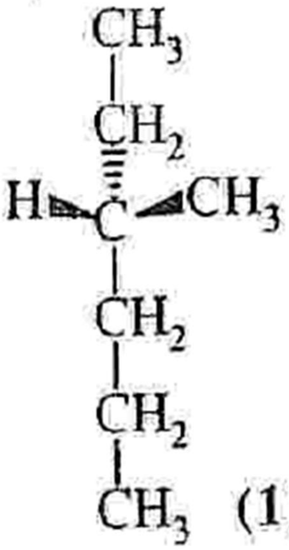


(1)

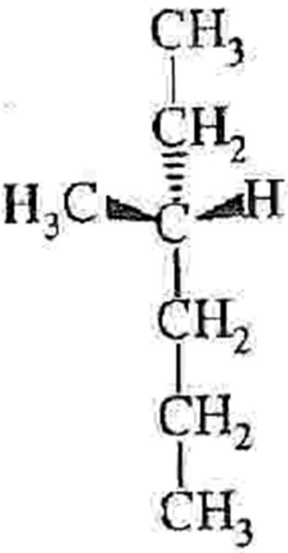


(2)

(g)

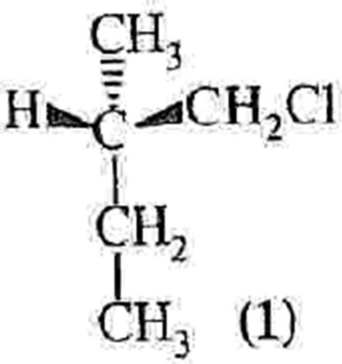


(1)

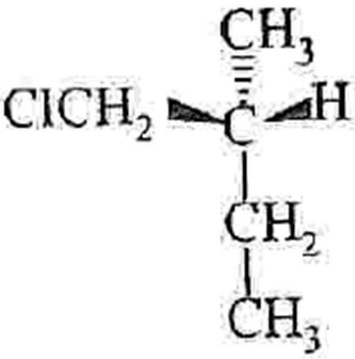


(2)

(h)



(1)

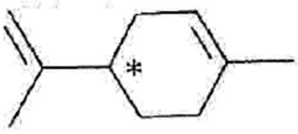


(2)

Problem 5.5

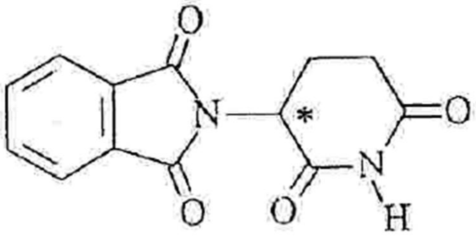
(a) Limonenin hangi atomu stereomerkezdir? (b) Talidomidin hangi atomu stereomerkezdir? Limonen ve talidomid enantiyomerleri için bağ çizgi formülleri çiziniz ve her birinin stereomerkezini kama-kesikli kama gösterimini (Altbölüm 1.17E) kullanarak gösteriniz.

5.5 (a)

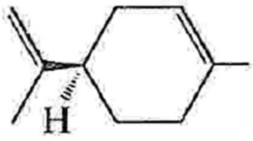


Limonene

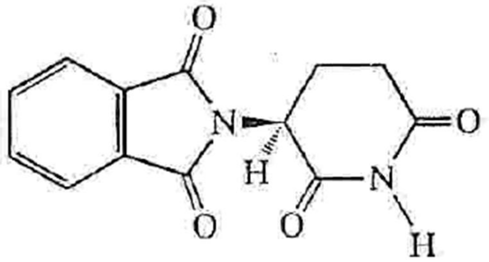
(b)



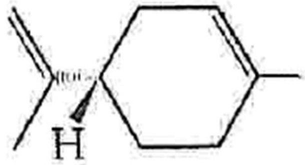
Thalidomide



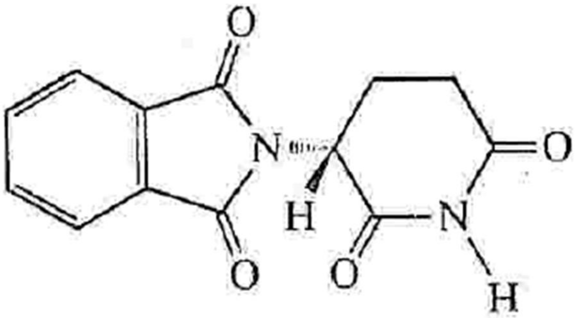
(*R*)



(*S*)



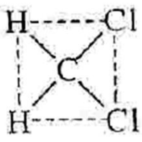
(*S*)



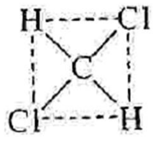
(*R*)

Problem 5.6 ➤ Disübstitüe metanların örneklerinden CH_2Cl_2 ve CH_2BrCl'yi göz önüne alarak yapacağınız incelemeden bu karbon bileşikleri için kare düzlem yapıların niçin mümkün olamayacağını gösteriniz. (a) Eğer karbon kare düzlem bir yapıya sahip olsaydı her birinde kaç tane izomer mümkün olurdu? (b) Karbon düzgün dörtyüzlü ise, her birinde kaç izomer mümkün olur? (c) ve (d) Şıkları için trisübstitüe bir metan örneği olarak CHBrClF yi göz önüne alınız. (c) Karbon, kare düzlem bir yapıya sahip olsaydı kaç tane izomer mümkün olurdu? (d) Karbon düzgün dörtyüzlü ise, CHBrClF için kaç kaç izomer mümkün olur?

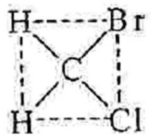
5.6 (a) Two in each instance.



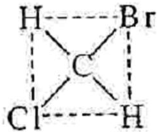
and



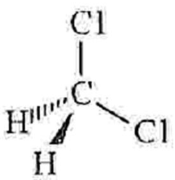
or



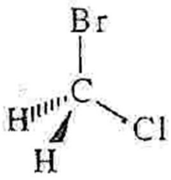
and



(b) Only one in each instance.

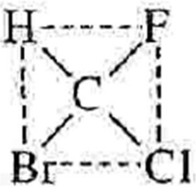


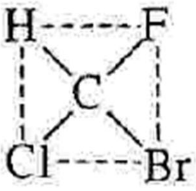
or



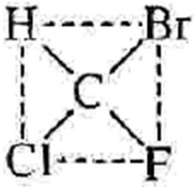
Any other tetrahedral arrangements will be superposable on one or the other of the above.

(c) Three:

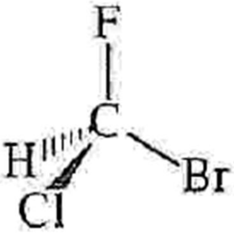




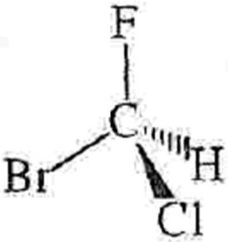
and



(d) Two:



and



Problem 5.1'de verilen nesnelerden simetri düzlemine sahip olan ve bu yüzden akiral olanlar hangileridir? ◄ **Problem 5.7**

5.7 The following items possess a plane of symmetry, and are, therefore, achiral.

(a) A screwdriver

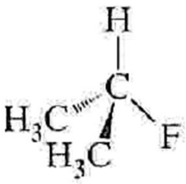
(b) A baseball bat (ignoring any writing on it)

(h) A hammer

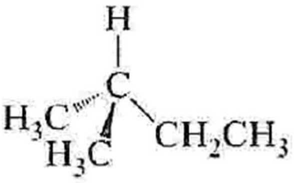
Problem 5.4'teki akiral moleküllerin hepsinin üç boyutlu formüllerini yazınız ve bir simetri düzlemi tasarımı yapınız. (Bir simetri düzlemi tasarımı yapabilmek için molekülü uygun bir konformasyonda yazmalısınız. Bu tasarım, yalnızca oda sıcaklığında serbestçe dönebilen birli bağlara ve birli bağlarla birleşmiş gruplara sahip olduklarından bu moleküllerin hepsi için uygundur. Bu konuyu Altbölüm 5.11'de daha ayrıntılı olarak tartışacağız.) ◄ **Problem 5.8**

5.8 In each instance below, the plane defined by the page is a plane of symmetry.

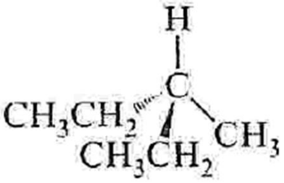
(a)



(b)

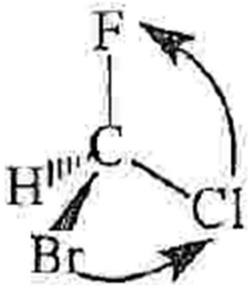


(f)

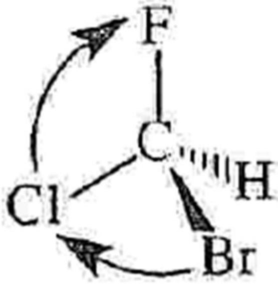


Bromokloroflorometanların enantiyomerik şekillerini yazınız ve her bir enantiyomeri doğru olarak (*R*) veya (*S*) gösterimi ile belirtiniz. ◄ **Problem 5.9**

5.9



(*S*)



(*R*)

Problem 5.10 Problem 5.4'e cevap olarak verilen her bir enantiyomer çifti için (*R*) ve (*S*) gösterimlerini belirtiniz.

5.10 (c) (1) is (*S*)
(2) is (*R*)

(d) (1) is (*S*)
(2) is (*R*)

(e) (1) is (*S*)
(2) is (*R*)

(g) (1) is (*S*)
(2) is (*R*)

(h) (1) is (*S*)
(2) is (*R*)

Problem 5.11 Aşağıdaki setlerin her birindeki sübstitüentleri öncelik sırasına göre en yüksekten en düşüğe doğru sıralayınız:

(a) $-Cl$, $-OH$, $-SH$, $-H$
(b) $-CH_3$, $-CH_2Br$, $-CH_2Cl$, $-CH_2OH$
(c) $-H$, $-OH$, $-CHO$, $-CH_3$
(d) $-CH(CH_3)_2$, $-C(CH_3)_3$, $-H$, $-CH{=}CH_2$
(e) $-H$, $-N(CH_3)_2$, $-OCH_3$, $-CH_3$

5.11 (a) $-Cl > -SH > -OH > -H$

(b) $-CH_2Br > -CH_2Cl > -CH_2OH > -CH_3$

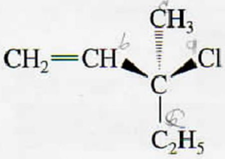
(c) $-OH > -CHO > -CH_3 > -H$

(d) $-C(CH_3)_3 > -CH{=}CH_2 > -CH(CH_3)_2 > -H$

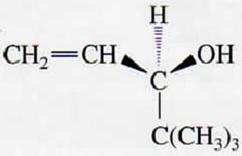
(e) $-OCH_3 > -N(CH_3)_2 > -CH_3 > -H$

Problem 5.12 Aşağıdaki bileşiklerin herbirini (*R*) veya (*S*) gösterimleri ile belirtiniz.

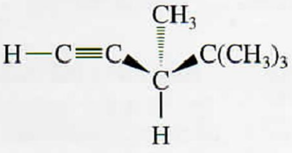
(a)



(b)

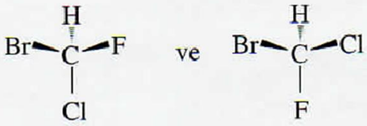


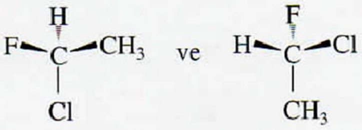
(c)

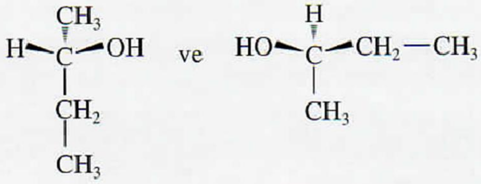


5.12 (a) (*S*) (b) (*R*) (c) (*S*)

Problem 5.13 ➤ Her çiftteki iki yapının enantiyomerleri mi yoksa aynı bileşiğin farklı yönlenmelerdeki iki molekülünü mü temsil ettiğini söyleyiniz.

(a) 
$\begin{array}{c} H \\ Br-C-F \\ Cl \end{array}$ ve $\begin{array}{c} H \\ Br-C-Cl \\ F \end{array}$

(b) 
$\begin{array}{c} H \\ F-C-CH_3 \\ Cl \end{array}$ ve $\begin{array}{c} F \\ H-C-Cl \\ CH_3 \end{array}$

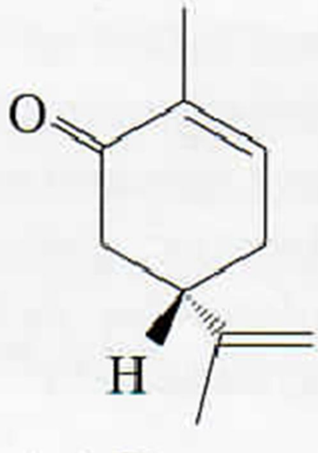
(c) 
$\begin{array}{c} CH_3 \\ H-C-OH \\ CH_2 \\ CH_3 \end{array}$ ve $\begin{array}{c} H \\ HO-C-CH_2-CH_3 \\ CH_3 \end{array}$

5.13 (a) Enantiomers

(b) Two molecules of the same compound

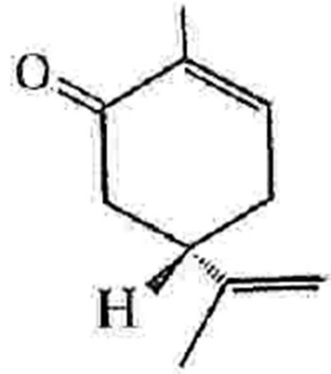
(c) Enantiomers

Problem 5.14 Aşağıda (+)-karvonun konfigürasyonu görülüyor. (+)-Karvon, kimyon tohumu yağının ana bileşenidir ve yağın karakteristik kokusundan sorumludur. Onun enantiyomeri olan (–)-karvon, nane yağının ana bileşenidir ve bunun karakteristik kokusunu verir. Karvon enantiyomerlerinin aynı şekilde kokmaması gerçeği bu bileşikleri algılayan burundaki algılayıcı kısımların kiral olduğunu, uygun bir enantiyomerin kendine özgü bir kısıma uyacağını düşündürür (tıpkı bir elin, tam uygun şekilde yerleşmesi için doğru kiralliğe sahip bir eldivene ihtiyaç duyması gibi). (+)- ve (–)-Karvonların *R* ve *S* tanımlamalarını yapınız.

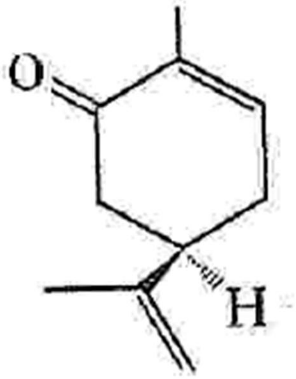


(+)-Karvon

5.14



(*S*)-(+)-Carvone



(*R*)-(−)-Carvone

Problem 5.15 ➤ Bir 2-metil-1-bütanol numunesi (bkz. Altbölüm 5.7C) + 1,151°'lik bir özgül çevirmeye, $[\alpha]_D^{25}$, sahiptir. (a) Bu numunenin % enantiyomerik fazlalığı nedir? (b) Hangi enantiyomer fazla olarak bulunur? (*R*) mi, yoksa (*S*) mi?

5.15 (a)

$$\text{Enant. Excess} = \frac{\text{observed rotation}}{\text{specific rotation of pure enantiomer}} \times 100$$

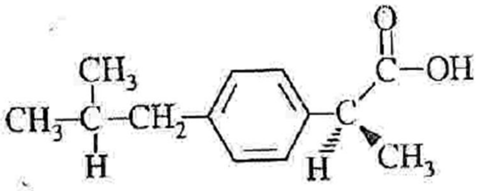
$$= \frac{+1.151^\circ}{+5.756^\circ} \times 100$$

$$= 20.00\%$$

(b) since the (*R*) enantiomer (see Section 5.7C) is +, the (*R*) enantiomer is present in excess.

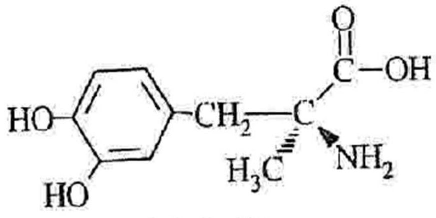
Problem 5.16 ➤ (a) İbuprofen, (b) metildopa ve (c) penisilaminin (*S*) izomerlerinin üç boyutlu formüllerini yazınız.

5.16 (a)



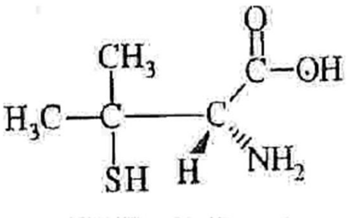
(*S*)-Ibuprofen

(b)



(*S*)-Methyldopa

(c)



(*S*)-Penicillamine

(a) **3** ve **4** enantiyomerse **1** ve **4** ne olur? (b) **2** ile **3** ve **2** ile **4** ne olur? (c) **1** ve **3**'ün aynı erime noktasına sahip olmasını bekler misiniz? (d) Kaynama noktaları aynı mıdır? (e) Buhar basınçları aynı mıdır? ◄ **Problem 5.17**

5.17 (a) Diastereomers.

(b) Diastereomers in each instance.

(c) No, diastereomers have different melting points.

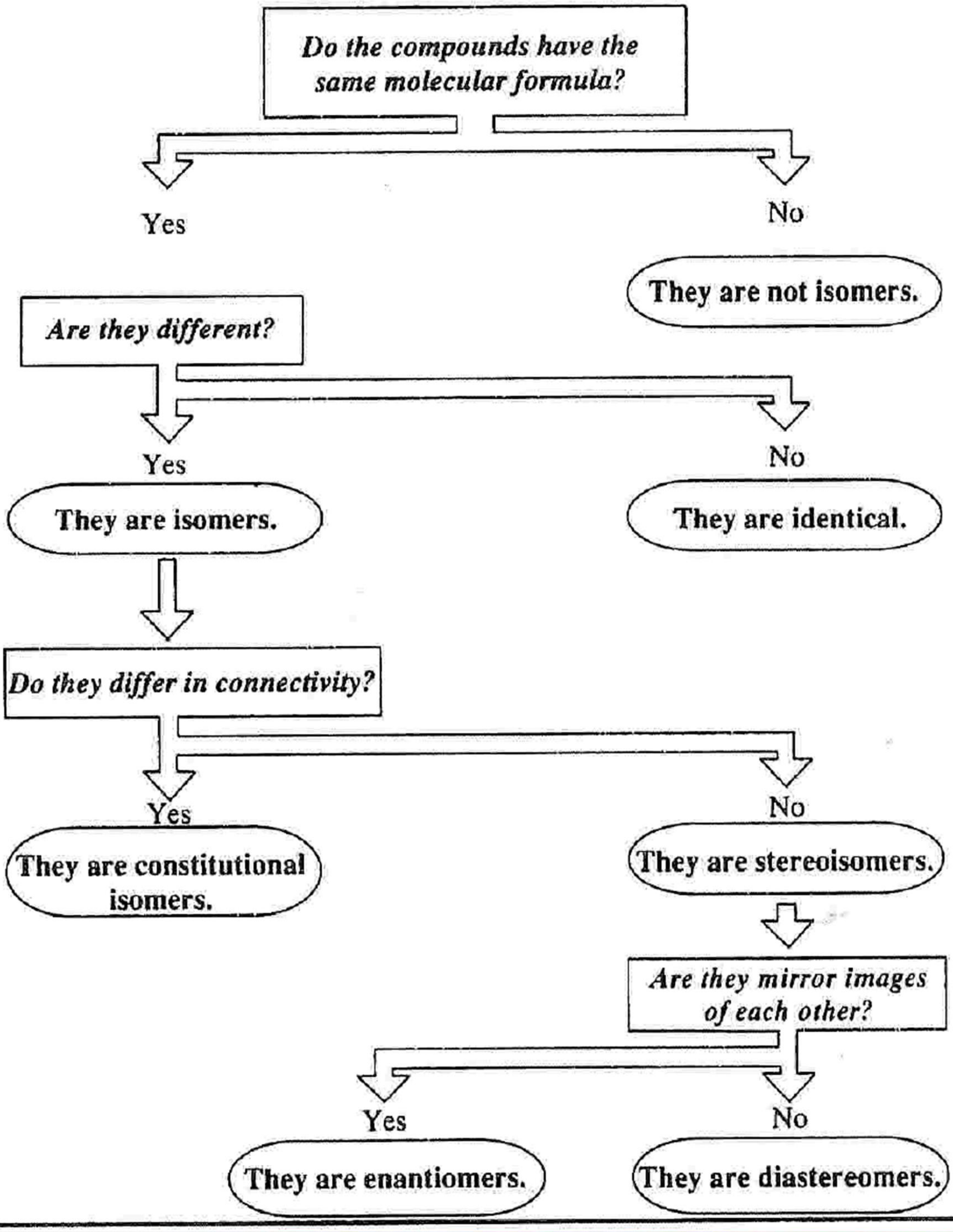
(d) No, diastereomers have different boiling points.

(e) No, diastereomers have different vapor pressures.

STUDY AID

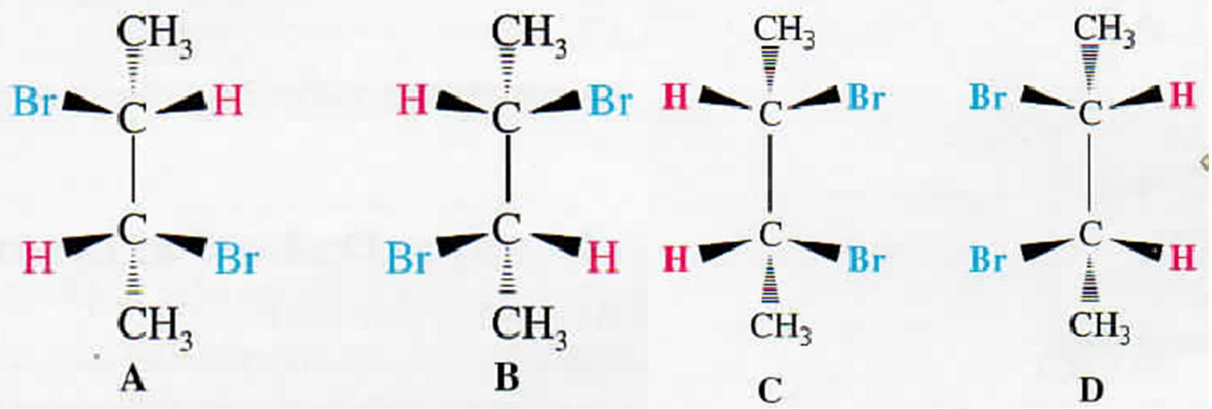
An Approach to the Classification of Isomers

We can classify isomers by asking and answering a series of questions:



Problem 5.18 ➤ Aşağıdakilerden hangileri optikçe aktif olabilir?

(a) Saf **A** numunesi
(b) Saf **B** numunesi
(c) Saf **C** numunesi
(d) **A** ve **B**'nin eşmolar karışımı



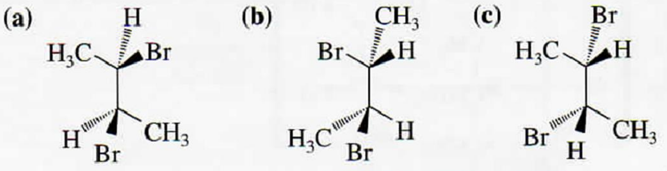
5.18 (a) It would be optically active.

(b) It would be optically active.

(c) No, because it is a meso compound.

(d) No, because it would be a racemic form.

Problem 5.19 ➤ Aşağıda, üç bileşik için çakışık olmayan konformasyonda yazılmış formüller görüyorsunuz. Her bir örnekte, her bir formülün temsil ettiği bileşiğin hangisi (**A**, **B** veya **C**) olduğunu söyleyiniz.



5.19 (a) Represents A

(b) Represents C

(c) Represents B

Problem 5.20 ➤ Aşağıdaki bileşiklerin her birinin bütün stereoizomerleri için üç boyutlu formüller yazınız. Enantiyomer çiftlerini ve mezo bileşikleri işaretleyiniz.

(a) $CH_3CHClCHClCH_3$

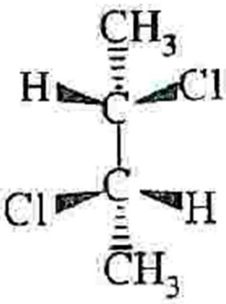
(b) $CH_3CHOHCH_2CHOHCH_3$

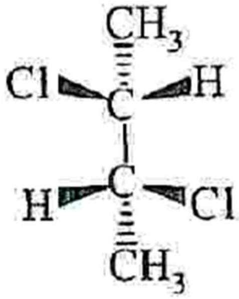
(c) $CH_2ClCHFCHFCH_2Cl$

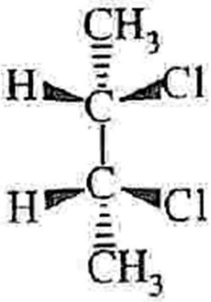
(d) $CH_3CHOHCH_2CHClCH_3$

(e) $CH_3CHBrCHFCH_3$

5.20 (a)


(1)

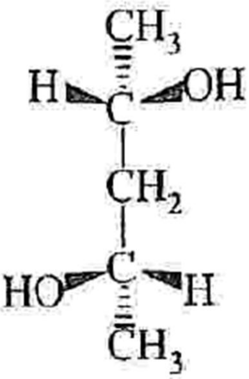

(2)

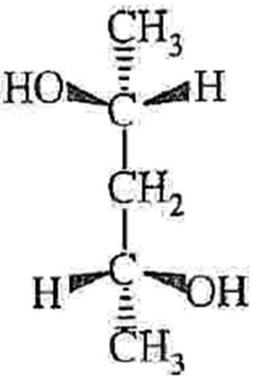

(3)

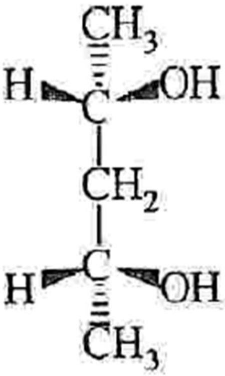
Enantiomers

Meso compound

(b)


(1)

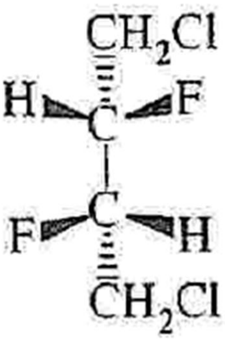

(2)

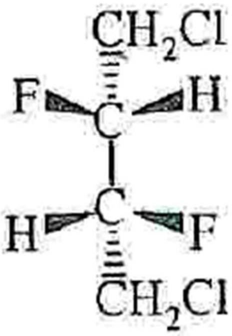

(3)

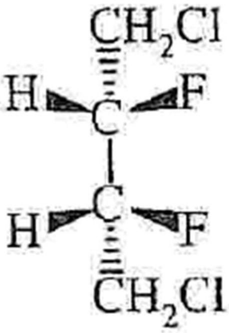
Enantiomers

Meso compound

(c)


(1)

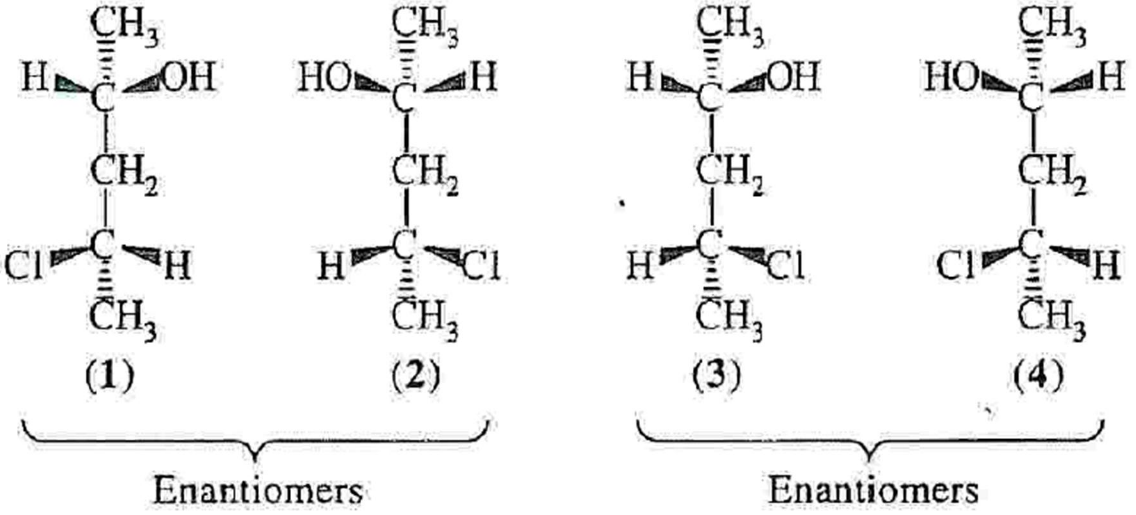

(2)


(3)

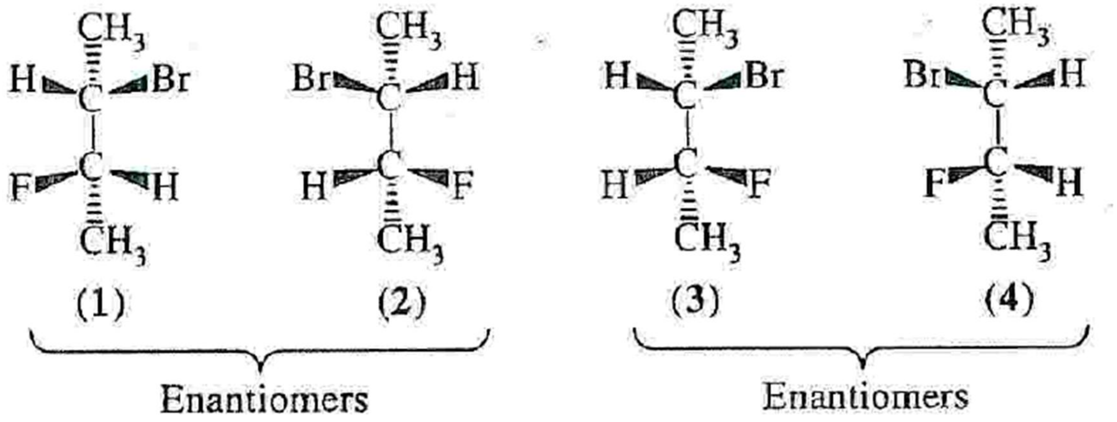
Enantiomers

Meso compound

(d)



(e)



Altbölüm 5.11A'daki **B** ve **C** bileşikleri için *R* ve *S* tanımlamalarını içeren isimler veriniz. ➤ **Problem 5.21**

5.21 B is (2*S*,3*S*)-2,3-Dibromobutane
C is (2*R*,3*S*)-2,3-Dibromobutane

Problem 5.20'ye verdiğiniz cevaplar için (*R*) ve (*S*) tanımlamalarını içeren isimler veriniz. ➤ **Problem 5.22**

5.22 (a) (1) is (2*S*,3*S*)-2,3-Dichlorobutane
(2) is (2*R*,3*R*)-2,3-Dichlorobutane
(3) is (2*R*,3*S*)-2,3-Dichlorobutane

(b) (1) is (2*S*,4*S*)-2,4-Pentanediol
(2) is (2*R*,4*R*)-2,4-Pentanediol
(3) is (2*R*,4*S*)-2,4-Pentanediol

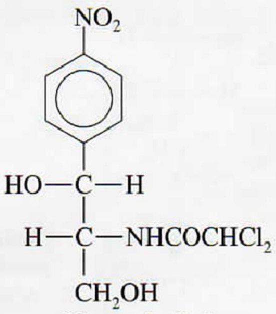
(c) (1) is (2*R*,3*R*)-1,4-Dichloro-2,3-difluorobutane
(2) is (2*S*,3*S*)-1,4-Dichloro-2,3-difluorobutane
(3) is (2*R*,3*S*)-1,4-Dichloro-2,3-difluorobutane

(d) (1) is (2*S*,4*S*)-4-Chloro-2-pentanol
(2) is (2*R*,4*R*)-4-Chloro-2-pentanol
(3) is (2*S*,4*R*)-4-Chloro-2-pentanol
(4) is (2*R*,4*S*)-4-Chloro-2-pentanol

(e) (1) is (2*S*,3*S*)-2-Bromo-3-fluorobutane
(2) is (2*R*,3*R*)-2-Bromo-3-fluorobutane
(3) is (2*S*,3*R*)-2-Bromo-3-fluorobutane
(4) is (2*R*,3*S*)-2-Bromo-3-fluorobutane

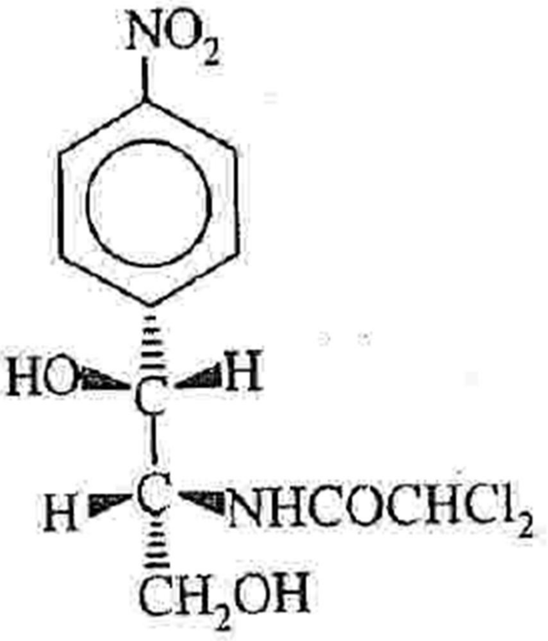
Problem 5.23

Kloramfenikol (aşağıda), özellikle tifo ateşine karşı etkin olan, *Streptomyces venezuelae*'den izole edilen etkili bir antibiyotiktir. Bir aromatik halkaya bağlanmış bir nitro (–NO_2) grubu içerdiği gösterilen ilk doğal maddedir. Kloramfenikoldeki her iki stereomerkezin de (*R*) konfigurasyona sahip olduğu bilinir. İki stereomerkezi belirleyin ve kloramfenikol için üç boyutlu bir formül yazınız.



Kloramfenikol

5.23



Chloramphenicol

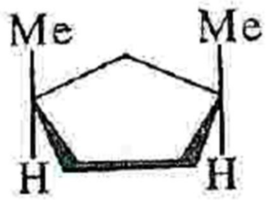
(a) *trans*-1,2-Dimetilsiklopentan (**5**) ayna görüntüsüyle (yani bileşik **6** ile) çakışır mı? (b) *cis*-1,2-Dimetilsiklopentan (7), ayna görüntüsüyle çakışır mı? (c) *cis*-1,2-Dimetilsiklopentan kiral bir molekül müdür? (d) *cis*-1,2-Dimetilsiklopentan optikçe aktiflik gösterir mi? (e) **5** ve **7** arasındaki stereoizomerik ilişki nedir? (f) **6** ve **7** arasındaki stereoizomerik ilişki nedir? ◀ **Problem 5.24**

5.24 (a) No (b) Yes (c) No (d) No (e) Diastereomers

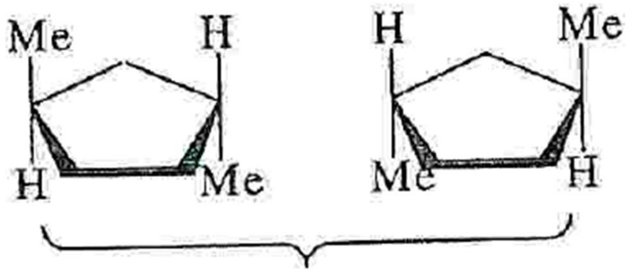
(f) Diastereomers

1,3-Dimetilsiklopentanın bütün stereoizomerleri için yapı formüllerini yazınız. Eğer varsa, enantiyomer çiftlerini ve mezo bileşikleri işaretleyiniz. ◀ **Problem 5.25**

5.25



Meso compound



Enantiomers

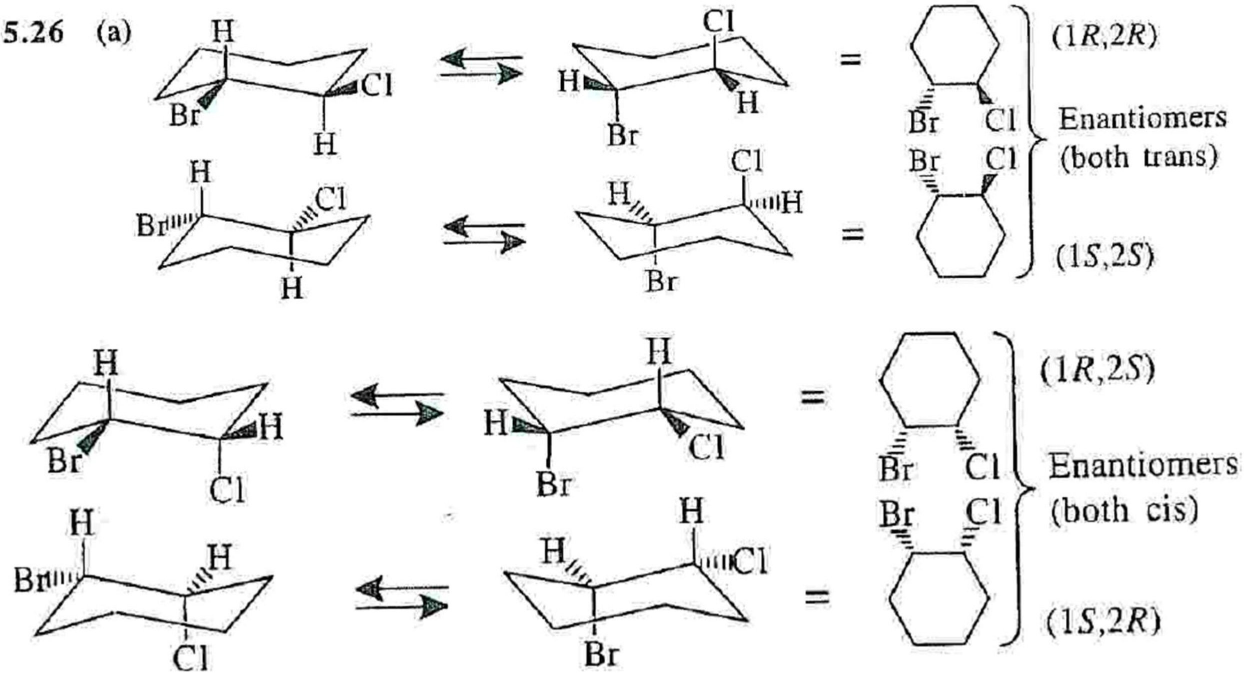
Aşağıdakilerin her birinin bütün izomerleri için formüller yazınız. Varsa, enantiyomer çiftlerini ve akiral bileşikleri tanımlayınız. ◀ **Problem 5.26**

(a) 1-Bromo-2-klorosikloheksan

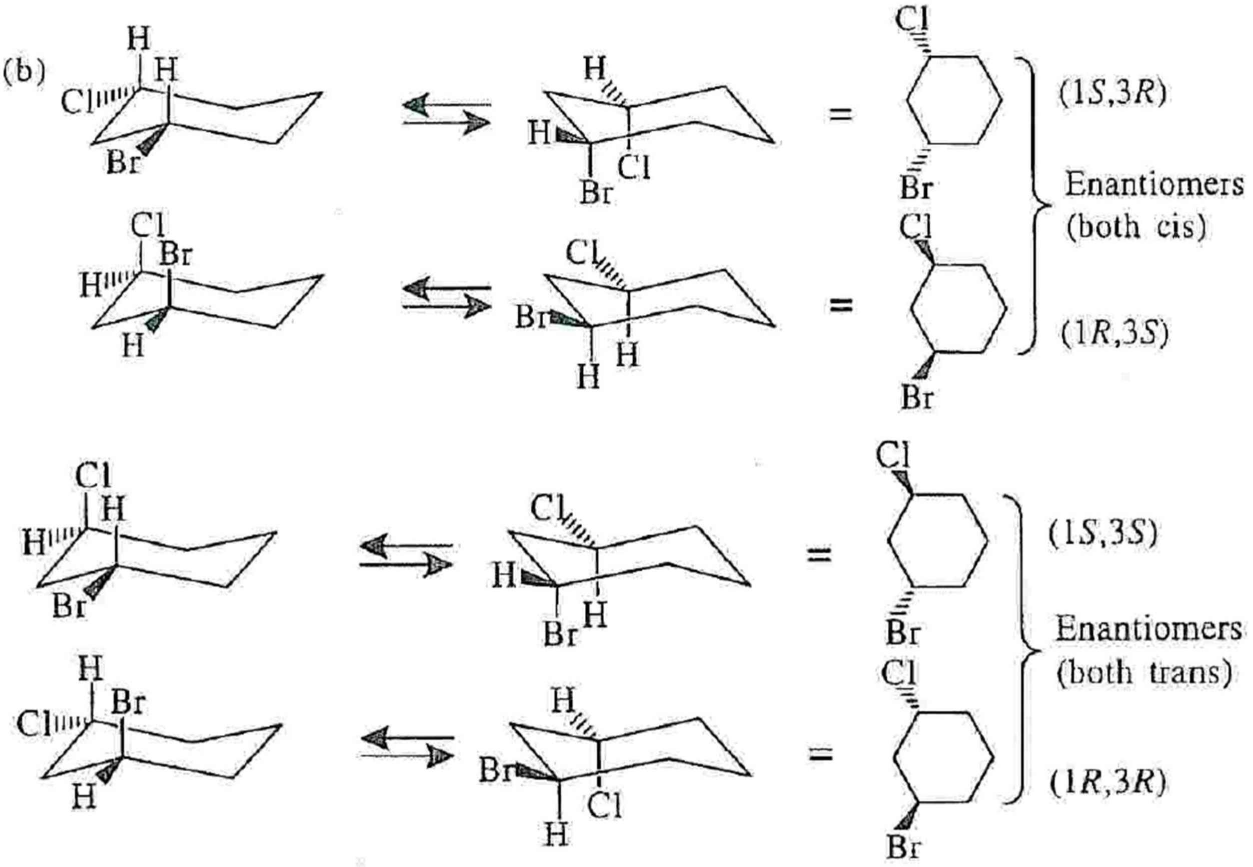
(b) 1-Bromo-3-klorosikloheksan

(c) 1-Bromo-4-klorosikloheksan

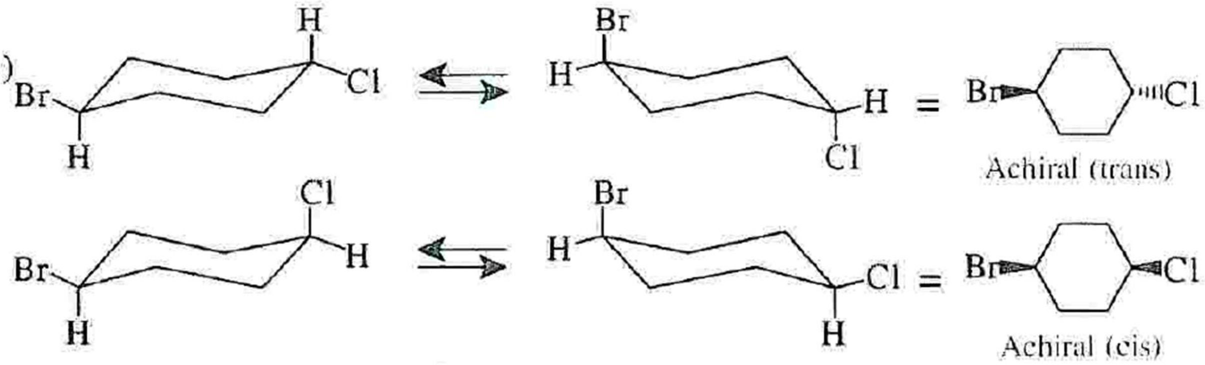
5.26 (a)



(b)



(c)

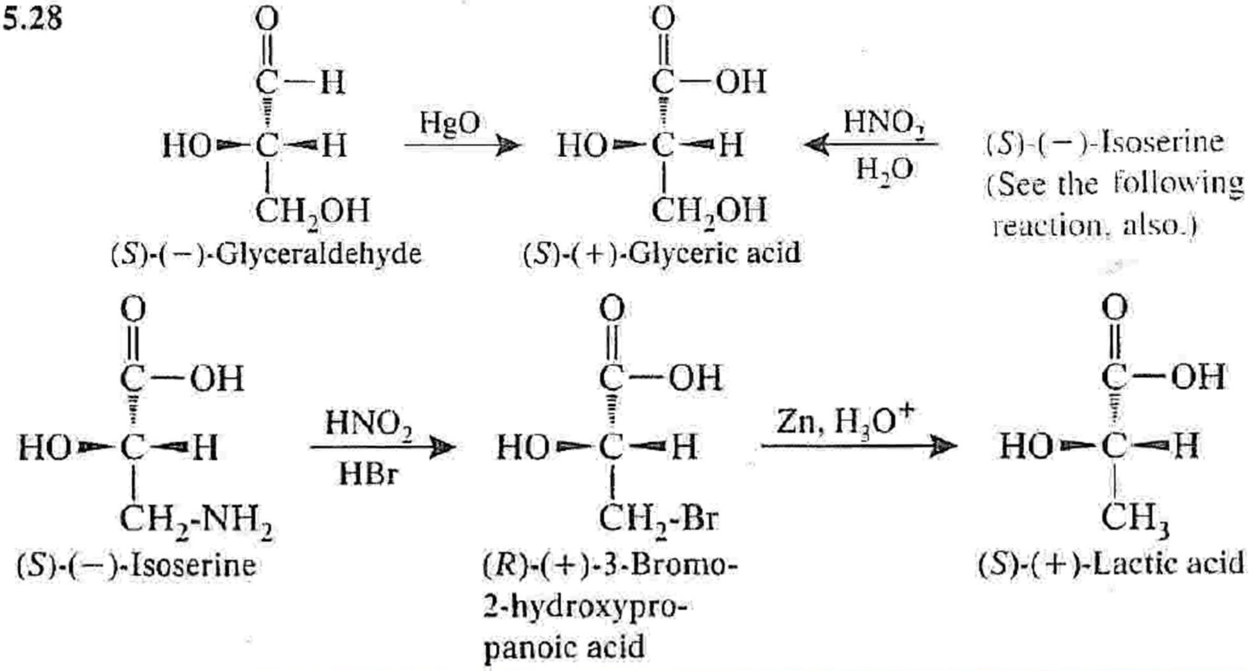


Problem 5.26'ya verdiğiniz cevaplarda, her bir bileşik için (*R*–*S*) tanımlanmasını yapınız. ➤ **Problem 5.27**

5.27 See Problem 5.26. The molecules in (c) are achiral, so they have no (*R-S*) designation.

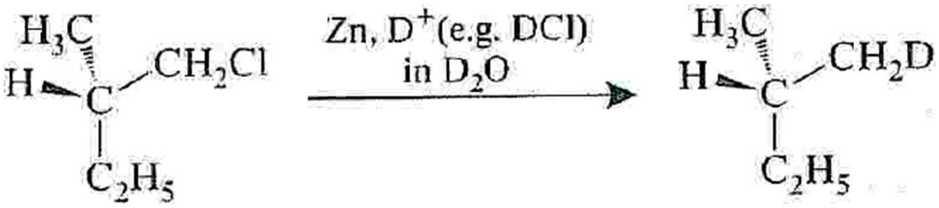
Problem 5.28 ➤ (–)-Gliseraldehitin konfigürasyonuyla (+)-laktik asiti ilişkilendiren, yukarıdakine benzer bir sentezde başlangıç bileşiği, ürün ve bütün ara ürünler için üç boyutlu formülleri yazınız. Her bir bileşiğin doğru olarak (*R*)–(*S*) ve (+)-(–) tanımlamasını yapınız.

5.28



Problem 5.29 ➤ (*R*)-1-Dötero-2-metilbütanı nasıl sentezlersiniz? [*İpucu:* Altbölüm 5,7C'deki 1-kloro-2-metilbütanın enantiyomerlerinden birini başlangıç maddesi olarak ele alınız]

5.29



(*S*)-(+)-1-Chloro-2-methylbutane

(*R*)-1-Deuterio-2-methylbutane

5.30 Aşağıdakilerden hangileri kiraldir ve bu nedenle bir enantiyomer çifti olarak bulunabilir?

(a) 1,3-Diklorobütan
(b) 1,2-Dibromopropan
(c) 1,5-Dikloropentan
(d) 3-Etilpentan
(e) 2-Bromobisiklo[1.1.0]bütan
(f) 2-Florobisiklo[2.2.2]oktan
(g) 2-Klorobisiklo[2.1.1]heksan
(h) 5-Klorobisiklo[2.1.1]heksan

5.30 (a), (b), (f) and (g) only

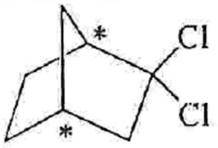
5.31 **(a)** Enantiyomerik yapılarda bulunabilmesi için bir alkan (sikloalkan değil) kaç karbon atomuna sahip olmalıdır? **(b)** Karbon atomlarının en az sayıda olduğu bu iki enantiyomer seti için doğru adları yazınız.

5.31 (a) Seven.

(b) (*R*)- and (*S*)-3-Methylhexane and (*R*)- and (*S*)-2,3-dimethylpentane.

5.32 **(a)** 2,2-Diklorobisiklo[2.2.1]heptanın yapısını yazınız. **(b)** Bu bileşik kaç tane stereomerkez içeriyor? **(c)** 2^n Kuralına göre kaç tane stereoizomer tahmin edersiniz? **(d)** 2,2-Diklorobisiklo[2.2.1]heptan için yalnızca bir enantiyomer çifti mümkündür. Açıklayınız.

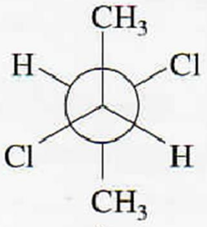
5.32 (a) and (b)



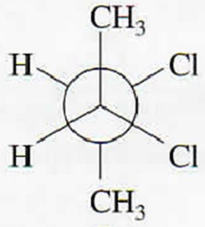
(c) Four

(d) Because a trans arrangement of the one carbon bridge is structurally impossible. Such a molecule would have too much strain.

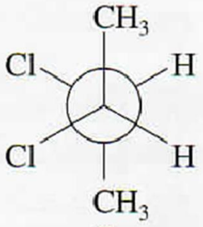
5.33 (*R*,*R*)-, (*S*,*S*)- ve (*R*,*S*)-2,3-Diklorobütan için Newman izdüşüm formülleri aşağıda görülmektedir. **(a)** Hangi formül, hangisinindir? **(b)** Hangi formül bir mezo bileşiğidir?



A



B



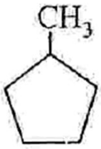
C

5.33 (a) **A** is (*R*,*S*)-2,3-dichlorobutane; **B** is (*S*,*S*)-2,3-dichlorobutane; **C** is (*R*,*R*)-2,3-dichlorobutane.

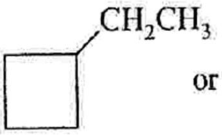
(b) **A**

5.34 Aşağıdaki şıkların her biri için uygun formülleri yazınız. **(a)** Sikloheksanın yapı izomeri olan halkalı bir molekül, **(b)** C_6H_{12} formülünde, bir halka içeren ve birbirinin enantiyomeri olan moleküller, **(c)** C_6H_{12} formülünde, bir halka içeren ve birbirinin diastereomeri olan moleküller, **(d)** C_6H_{12} formülünde, halka içermeyen ve birbirinin enantiyomeri olan moleküller, **(e)** C_6H_{12} formülünde, halka içermeyen ve birbirinin diastereomeri olan moleküller.

5.34 (a)



or



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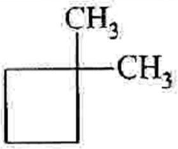
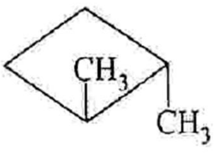
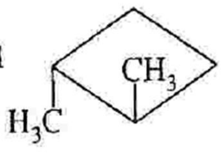


etc.

(b)



and



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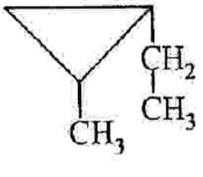

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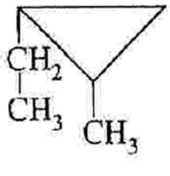
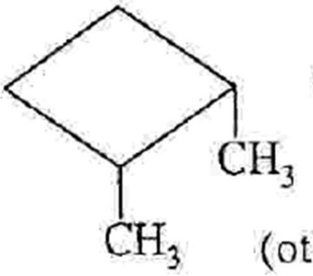
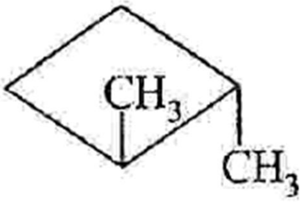


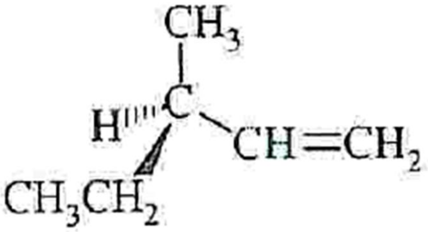
(other answers are possible)

(c)


and



(other answers are possible)

(d)


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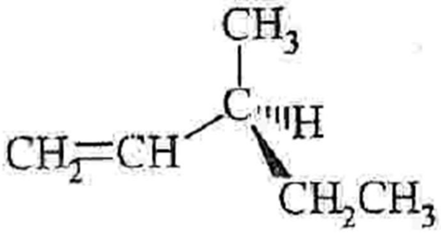
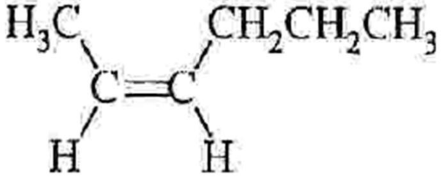


(e)


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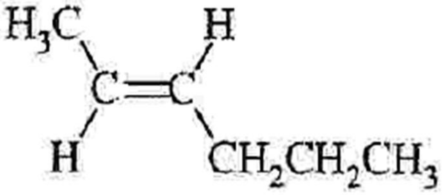
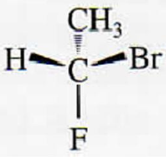
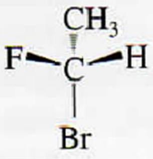


(other answers are possible)

5.35 Aşağıdaki yapı çiftlerini gözönüne alınız. Enantiyomerler, diastereomerler, yapı izomerleri veya aynı bileşiğin iki molekülü şeklinde tanımlayarak onlar arasındaki ilişkiyi belirleyiniz.

(a)


ve



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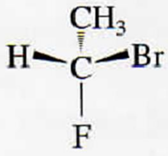

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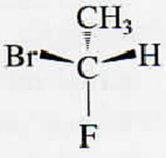

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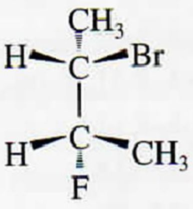

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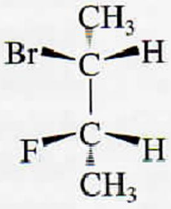

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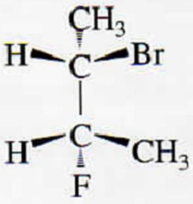

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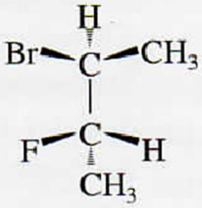

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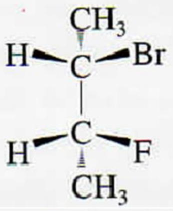

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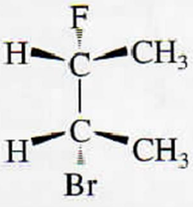

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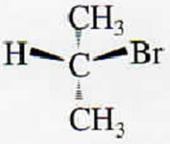

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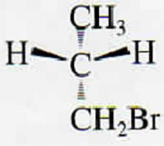

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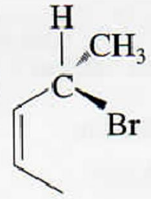

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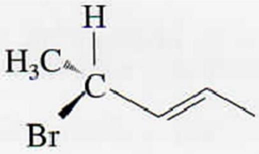

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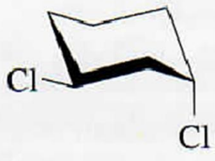

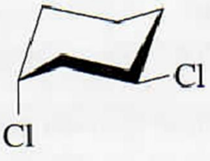

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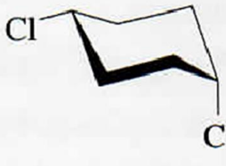

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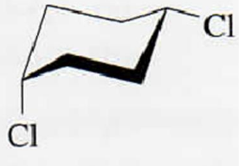

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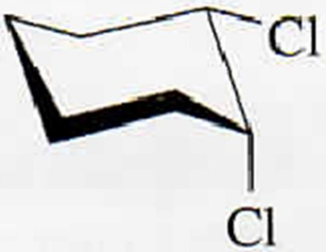

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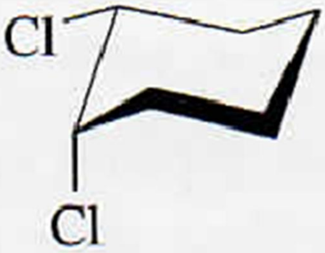

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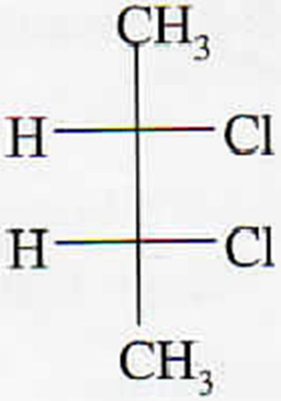

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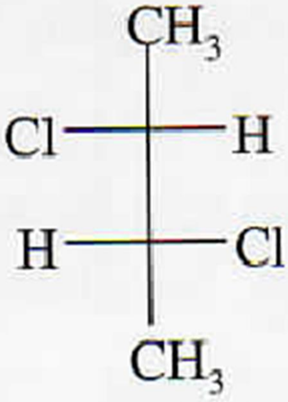
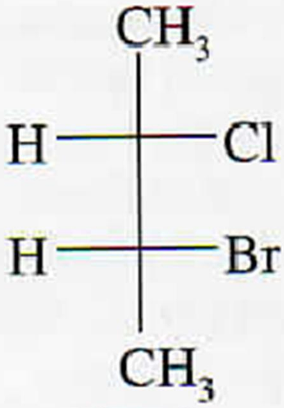


(l)



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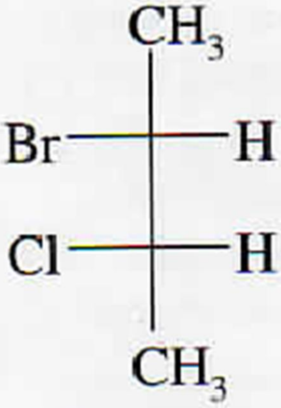

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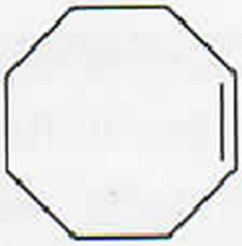

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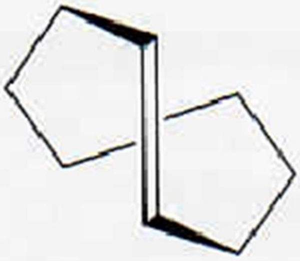

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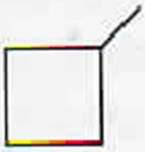

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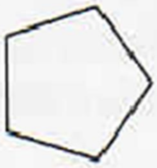
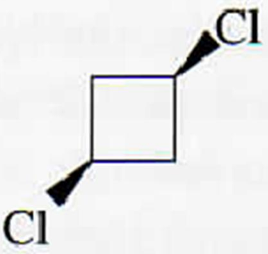


(o)



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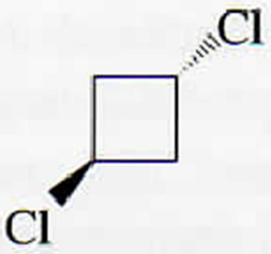
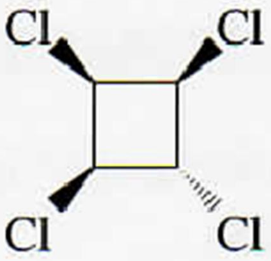


(p)



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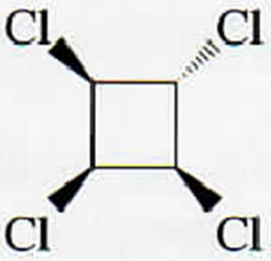
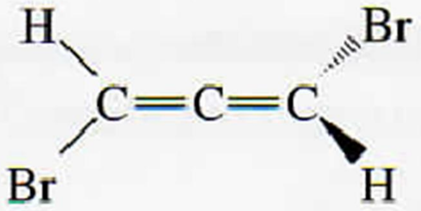


(q)



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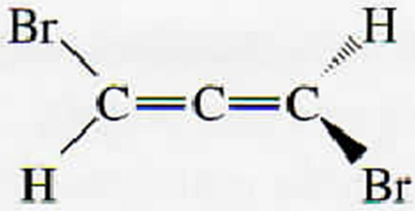


5.35 (a) Same

(b) Enantiomers

(c) Diastereomers

(d) Same

(e) Same

(f) Constitutional isomers

(g) Diastereomers

(h) Enantiomers

(i) Same

(j) Enantiomers that are interconvertible by a ring flip

(k) Diastereomers

(l) Same

(m) Diastereomers

(n) Constitutional isomers

(o) Diastereomers

(p) Same

(q) Same

5.36 Aşağıdaki bileşiklerin her birinin tahmin edilen stereokimyasını tartışınız.

(a) $ClCH{=}C{=}C{=}CHCl$ **(c)** $ClCH{=}C{=}C{=}CCl_2$

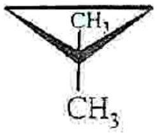
(b) $CH_2{=}C{=}C{=}CHCl$

5.36 All of these molecules are expected to be planar. Their stereochemistry is identical to that of the corresponding chloroethenes. (a) can exist as cis and trans isomers. Only one compound exists in the case of (b) and (c).

5.37 Dört dimetilsiklopropan izomeri vardır. **(a)** Bu izomerler için üç boyutlu formüller yazınız. **(b)** Hangi izomerler kiraldir? **(c)** Bu izomerlerin her birinin 1 molünü içeren bir karışım, basit bir gaz kromatografisine verilse, kaç kısım elde edilir ve her kısımda hangi bileşikler bulunur? **(d)** Bu kısımlardan kaç tanesi optikçe aktif olur?

5.37 (a)

(1)



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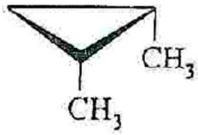
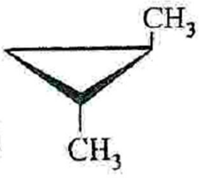


(3)



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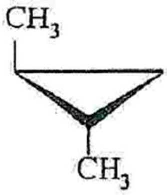


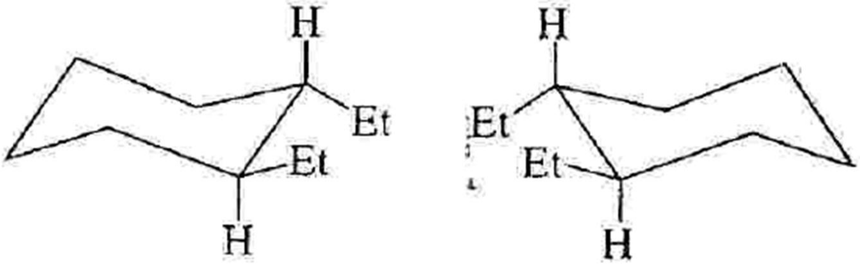
(b) (3) and (4) are chiral and are enantiomers of each other.

(c) Three fractions: a fraction containing (1), a fraction containing (2), and a fraction containing (3) and (4) [because, being enantiomers, (3) and (4) would have the same vapor pressure].

(d) None

5.38 (Bu problemi çözmek için model kullanınız.) **(a)** *trans*-1,2-Dietilsikloheksanın en kararlı konformasyonu için konformasyonel bir yapı ve onun ayna görüntüsünü yazınız. **(b)** Bu iki molekül çakışır mı? **(c)** Onlar bir halka "devrilmesiyle" birbirine dönüşür mü? **(d)** (a) Şıkkındaki işlemi *cis*-1,2-dietilsikloheksan için tekrarlayınız. **(e)** Bu moleküller çakışırlar mı? **(f)** Onlar birbirine dönüşebilir mi?

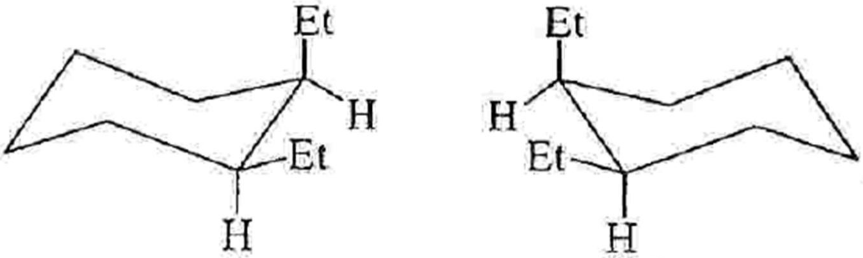
5.38 (a)



(b) No, they are not superposable.

(c) No, and they are, therefore, enantiomers of each other.

(d)

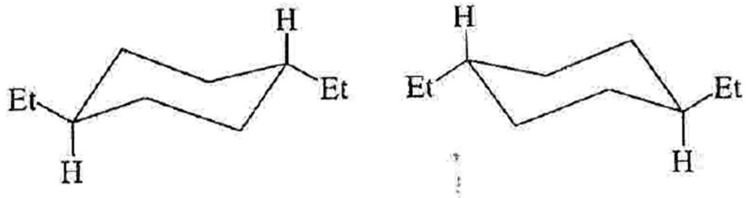


(e) No, they are not superposable.

(f) Yes, and they are, therefore, just different conformations of the same molecule.

5.39 (Bu problemi çözmek için model kullanınız.) **(a)** *trans*-1,2-Dietilsikloheksanın en kararlı konformasyonu için konformasyonel bir yapı ve onun ayna görüntüsünü yazınız. **(b)** Bu yapılar çakışır mı? **(e)** Onlar enantiyomerleri mi temsil ederler? **(d)** *trans*-1,2-Dietilsikloheksan bir stereoizomere sahip midir, ve eğer öyleyse, bu stereoizomer nedir? **(e)** Bu stereoizomer kiral mıdır?

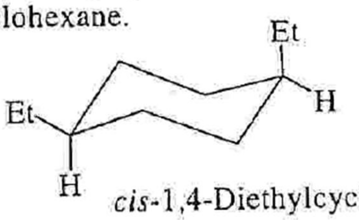
5.39 (a)



(b) Yes, and therefore *trans*-1.4-diethylcyclohexane is achiral.

(c) No, they are different orientations of the same molecule.

(d) Yes, *cis*-1,4-diethylcyclohexane is a stereoisomer (a diastereomer) of *trans*-1.4-diethylcyclohexane.

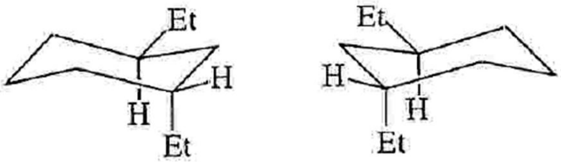


cis-1,4-Diethylcyclohexane

(e) No, it, too, is superposable on its mirror image. (Notice, too, that the plane of the page constitutes a plane of symmetry for both *cis*-1,4-diethylcyclohexane and for *trans*-1,4-diethylcyclohexane as we have drawn them.)

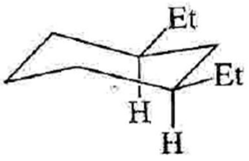
5.40 **(Bu problemi çözmek için model kullanınız.) 1,3-Dietilsikloheksanın stereoizomerlerinin hepsi için konformasyonel yapıları yazınız. Enantiyomer çiftlerini ve varsa mezo bileşiklerini işaretleyiniz.**

5.40 *trans*-1,3-Diethylcyclohexane can exist in the following enantiomeric forms.



trans-1,3-Diethylcyclohexane enantiomers

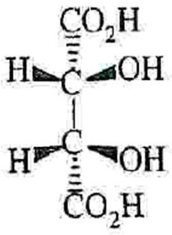
cis-1,3-Diethylcyclohexane consists of achiral molecules because they have a plane of symmetry. [The plane of the page (below) is a plane of symmetry.]



cis-1,3-Diethylcyclohexane

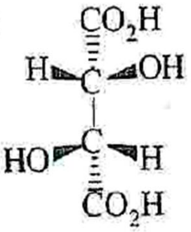
***5.41** Tartarik asit [$HO_2CCH(OH)CH(OH)CO_2H$], stereokimya tarihinde önemli bir bileşik olmuştur. Tartarik asitin doğal olarak bulunan iki şekli optikçe aktif değildir. Bir yapı 206°C, diğer yapı 140°C olan erime noktasına sahiptir. Erime noktası 206°C olan aktif olmayan tartarik asit, tartarik asitin optikçe aktif olan ve aynı erime noktasına sahip (170°C) iki şekline ayrılabilmektedir. Optikçe aktif tartarik asitlerden biri $[\alpha]_D^{25} = +12°$, diğeri $[\alpha]_D^{25} = -12°$ özgül çevirmeye sahiptir. Diğer aktif olmayan tartarik asiti optikçe aktif bileşiklere ayırmak için yapılan bütün girişimler başarısız olmuştur. **(a)** 140°C erime noktasına sahip tartarik asitin üç boyutlu yapısını yazınız. **(b)** Erime noktası 170°C tartarik asitler için mümkün yapılar nelerdir? **(c)** (b) Şıkkındaki tartarik asitlerin hangisinin pozitif çevirmeye ve hangisinin negatif çevirmeye sahip olduğundan emin olabilir misiniz? **(d)** Erime noktası 206°C olan tartarik asit şeklinin yapısı nedir?

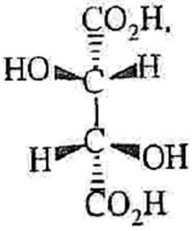
*5.41 (a) Since it is optically active and not resolvable, it must be the meso form:



(meso)

(b)





(c) No (d) A racemic modification

***5.42** **(a)** Saf bir X stereoizomerinin 589,6 nm'de ve 25°C'da 1,0 dm'lik tüp içerisinde 0,10 g/mL derişimindeki sulu çözeltisinin gözlenen çevirmesi –30°'dir. Bu sıcaklıkta maddenin özgül çevirmesi, $[\alpha]_D$, nedir? Hesaplayınız.

(b) Aynı koşullarda fakat 0,050 g/mL derişimdeki bir X çözeltisi, +165° çevirme göstermektedir. Bunun nasıl olabileceğini düşününüz? X stereoizomeri için $[\alpha]_D$'yi yeniden hesaplayınız.

(c) Yalnızca tek bir derişimde incelenen bir maddenin optik çevirmesi 0° ise tam olarak akiral olduğu söylenebilir mi? Yoksa rasemik midir?

*5.42 (a) $$[\alpha]_D = \frac{-30°}{(0.10\ g/mL)(1.0\ dm)} = -300°$$

(b) $$[\alpha]_D = \frac{+165°}{(0.05\ g/mL)(1.0\ dm)} = +3300°$$

The two rotation values can be explained by recognizing that this is a powerfully optically active substance and that the first reading, assumed to be −30°, was really +330°. Making this change the $[\alpha]_D$ becomes +3300° in both cases.

(c) No, the apparent 0° rotation could actually be + or −360° (or an integral multiple of these values).

***5.43** Eğer iki veya daha fazla stereomerkeze sahip saf bir madde numunesinin gözlenen çevirmesi 0° ise, o bir rasemat olabilir. Saf bir stereoizomer olabilir mi? Onun saf bir enantiyomer olması da mümkün müdür?

*5.43 Yes, it could be a *meso* form or an enantiomer whose stereocenters, by rare coincidence, happen to cancel each others activities.

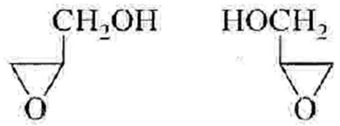
***5.44** Bilinmeyen bir Y maddesi $C_3H_6O_2$ molekül formülüne sahiptir. Bu madde, kırmızı ötesi ışımada 3200–3500 cm^{-1} bölgesinde soğurma yapan bir fonksiyonel gruba sahiptir (saf sıvı yani "katkısız" olarak incelendiğinde) ve 1620–1780 cm^{-1} bölgesinde hiçbir soğurma göstermemektedir. Y yapısındaki karbon atomlarının hiçbirine birden çok oksijen atomu bağlanmamıştır ve Y, iki (yalnızca iki) stereoizomerik yapı gösteriyor. Y'nin bu şekillerinin yapıları nelerdir?

*5.44 A compound $C_3H_6O_2$ has an index of hydrogen deficiency of 1. Thus, it could possess a carbon-carbon double bond, a carbon-oxygen double bond, or a ring.

The IR spectral data rule out a carbonyl group but indicate the presence of an —OH group.

No stable structure having molecular formula $C_3H_6O_2$ with a C=C bond can exist in stereoisomeric forms and 1,2-cyclopropanediol can exist in three stereoisomeric forms.

Only ethylene oxide (oxirane) derivatives are possible for Y:



İyonik Tepkimeler–Alkil Halojenürlerin Nükleofilik Yer Değiştirme ve Ayrılma Tepkimeleri

Çizelge 6.7 S_N1, S_N2, E1 ve E2 Tepkimelerinin Toplam Özeti

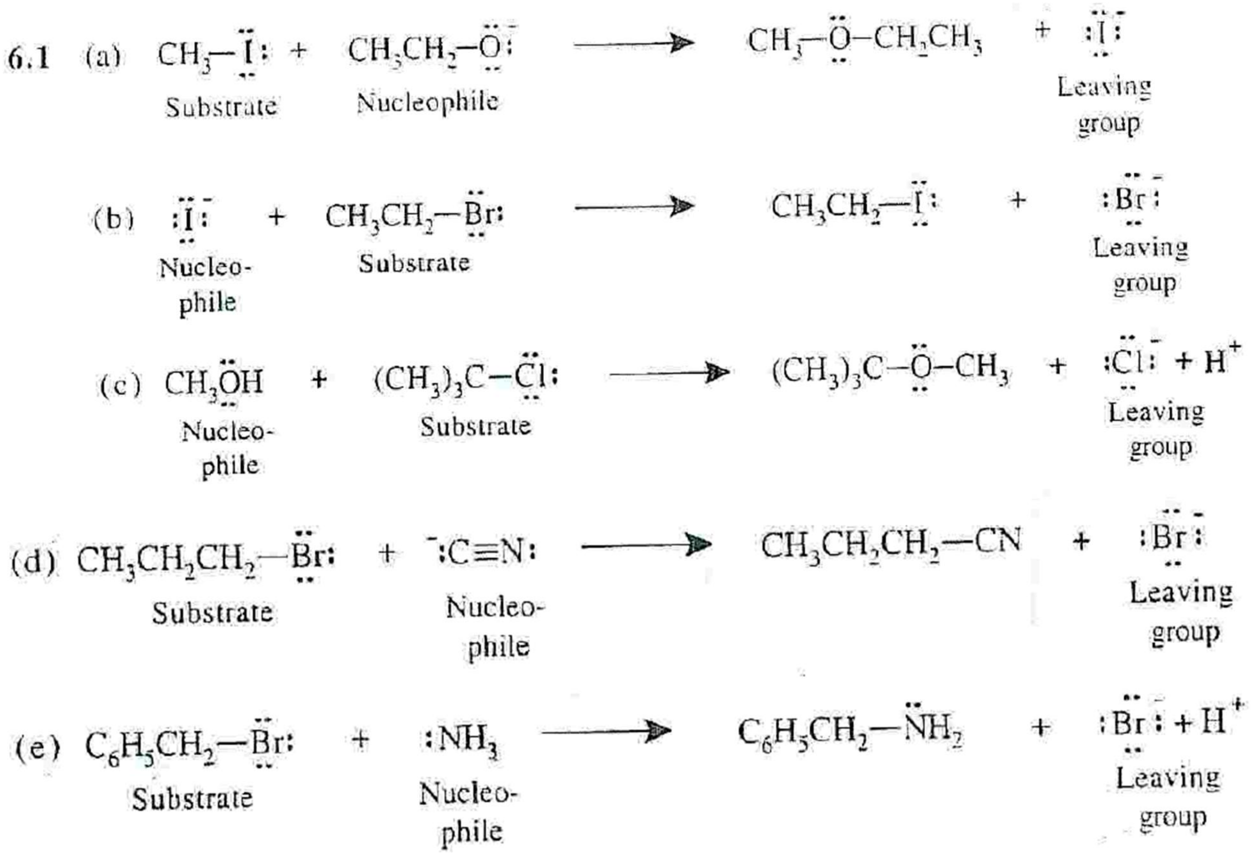
CH_3X	RCH_2X	$\overset{R}{\overset{\vert}{RCHX}}$	$R{-}\underset{R}{\overset{R}{C}}{-}X$
Metil	1°	2°	3°
	Yalnızca iki moleküllü tepkimeler		S_N1/E1 veya E2
S_N2 tepkimeleri verir	Hacimli ve güçlü bir baz [örneğin $(CH_3)_3CO^-$ gibi] kullanılmadığında başlıca S_N2, güçlü ve hacimli bazlar kullanıldığında da başlıca E2 verir	Zayıf bazlarla (örneğin I^-, CN^-, RCO_2^- gibi) başlıca S_N2 ve güçlü bazlarla (örneğin RO^- gibi) başlıca E2 verir	S_N2 Tepkimesi vermez. Solvoliz ile S_N1/E1 verir, ve düşük sıcaklıkta S_N1 yeğlenir. Güçlü bir baz kullanıldığı zaman [örneğin (RO^-) gibi] E2 baskındır.

Problem 6.1

Aşağıdaki tepkimeleri net iyonik tepkimeler olarak yazınız ve her bir tepkimede nükleofil, substrat ve ayrılan grubu gösteriniz.

(a) $CH_3I + CH_3CH_2ONa \longrightarrow CH_3OCH_2CH_3 + NaI$
(b) $NaI + CH_3CH_2Br \longrightarrow CH_3CH_2I + NaBr$
(c) $2\,CH_3OH + (CH_3)_3CCl \longrightarrow (CH_3)_3COCH_3 + CH_3OH_2^+ + Cl^-$
(d) $CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$
(e) $C_6H_5CH_2Br + 2\,NH_3 \longrightarrow C_6H_5CH_2NH_2 + NH_4Br$

6.1



(a) $\underset{\text{Substrate}}{CH_3{-}\ddot{\underset{..}{I}}:} + \underset{\text{Nucleophile}}{CH_3CH_2{-}\ddot{\underset{..}{O}}:^-} \longrightarrow CH_3{-}\ddot{\underset{..}{O}}{-}CH_2CH_3 + \underset{\text{Leaving group}}{:\ddot{\underset{..}{I}}:^-}$

(b) $\underset{\text{Nucleophile}}{:\ddot{\underset{..}{I}}:^-} + \underset{\text{Substrate}}{CH_3CH_2{-}\ddot{\underset{..}{Br}}:} \longrightarrow CH_3CH_2{-}\ddot{\underset{..}{I}}: + \underset{\text{Leaving group}}{:\ddot{\underset{..}{Br}}:^-}$

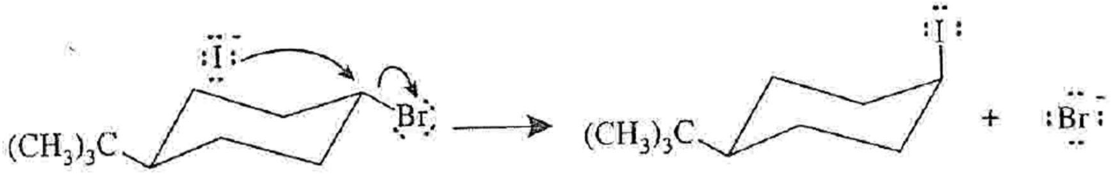
(c) $\underset{\text{Nucleophile}}{CH_3\ddot{\underset{..}{O}}H} + \underset{\text{Substrate}}{(CH_3)_3C{-}\ddot{\underset{..}{Cl}}:} \longrightarrow (CH_3)_3C{-}\ddot{\underset{..}{O}}{-}CH_3 + \underset{\text{Leaving group}}{:\ddot{\underset{..}{Cl}}:^-} + H^+$

(d) $\underset{\text{Substrate}}{CH_3CH_2CH_2{-}\ddot{\underset{..}{Br}}:} + \underset{\text{Nucleophile}}{^-:C{\equiv}N:} \longrightarrow CH_3CH_2CH_2{-}CN + \underset{\text{Leaving group}}{:\ddot{\underset{..}{Br}}:^-}$

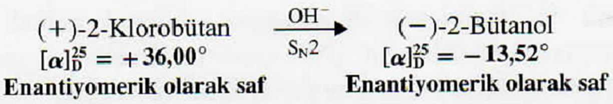
(e) $\underset{\text{Substrate}}{C_6H_5CH_2{-}\ddot{\underset{..}{Br}}:} + \underset{\text{Nucleophile}}{:NH_3} \longrightarrow C_6H_5CH_2{-}\ddot{N}H_2 + \underset{\text{Leaving group}}{:\ddot{\underset{..}{Br}}:^-} + H^+$

Sandalye konformasyonu yapılarını kullanınız (Altbölüm 4.12) ve *trans*-1-bromo-4-*ter*-bütilsikloheksanın iyodür iyonu ile verdiği tepkimede meydana gelen nükleofilik yer değiştirme tepkimesini gösteriniz (Reaktant ve ürünün en kararlı konformasyonunu gösteriniz.) ◄ **Problem 6.2**

6.2



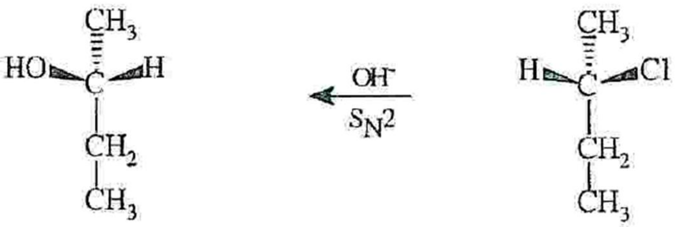
Problem 6.3 ➤ Tepkimenin *stereokimyasının* bilinmesi nedeniyle, molekül konfigürasyonları arasında bir ilişki kurmak için stereomerkezdeki bağın kırılmasını içeren S_N2 tepkimeleri kullanılabilir. (a) Aşağıdaki verilere dayanarak, 2-klorobütan enantiyomerlerinin konfigürasyonlarının belirlenmesiyle bunun nasıl doğrulanabileceğini gösteriniz. [(–)-2-Bütanolün konfigürasyonu Altbölüm 5.7C'de verilmiştir.]



$$\underset{\substack{[\alpha]_D^{25} = +36{,}00^\circ \\ \textbf{Enantiyomerik olarak saf}}}{(+)\text{-2-Klorobütan}} \xrightarrow[S_N2]{OH^-} \underset{\substack{[\alpha]_D^{25} = -13{,}52^\circ \\ \textbf{Enantiyomerik olarak saf}}}{(-)\text{-2-Bütanol}}$$

(b) Optikçe aktif (+)-2-klorobütan potasyum iyodür ile aseton içerisinde S_N2 tepkimesine maruz bırakıldığında, elde edilen 2-iyodobütan eksi çevirme gösterir. (–)-2-İyodobütanın konfigürasyonu nedir? (+)-2-İyodobütanınki nedir?

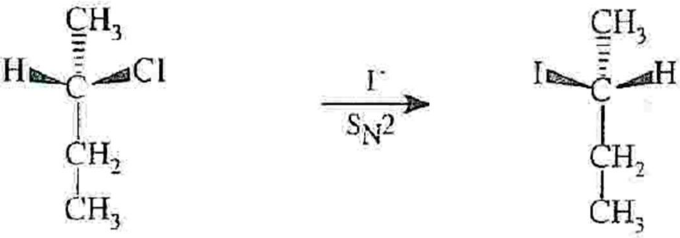
6.3 (a) We know that when a secondary alkyl halide reacts with hydroxide ion by substitution, the reaction occurs with *inversion of configuration* because the reaction is S_N2. If we know that the configuration of (−)-2-butanol (from Section 5.7C) is that shown here, then we can conclude that (+)-2-chlorobutane has the opposite configuration.



(*R*)-(-)-2-Butanol $[\alpha]^{25°}_{D} = -13.52°$

(*S*)-(+)-2-Chlorobutane $[\alpha]^{25°}_{D} = +36.00°$

(b) Again the reaction is S_N2. Because we now know the configuration of (+)-2-chlorobutane to be (*S*) [cf., part (a)], we can conclude that the configuration of (−)-2-iodobutane is (*R*).

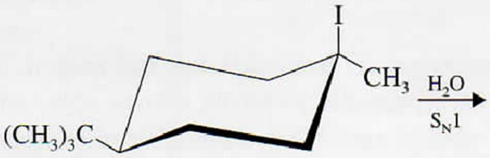


(*S*)-(+)-2-Chlorobutane

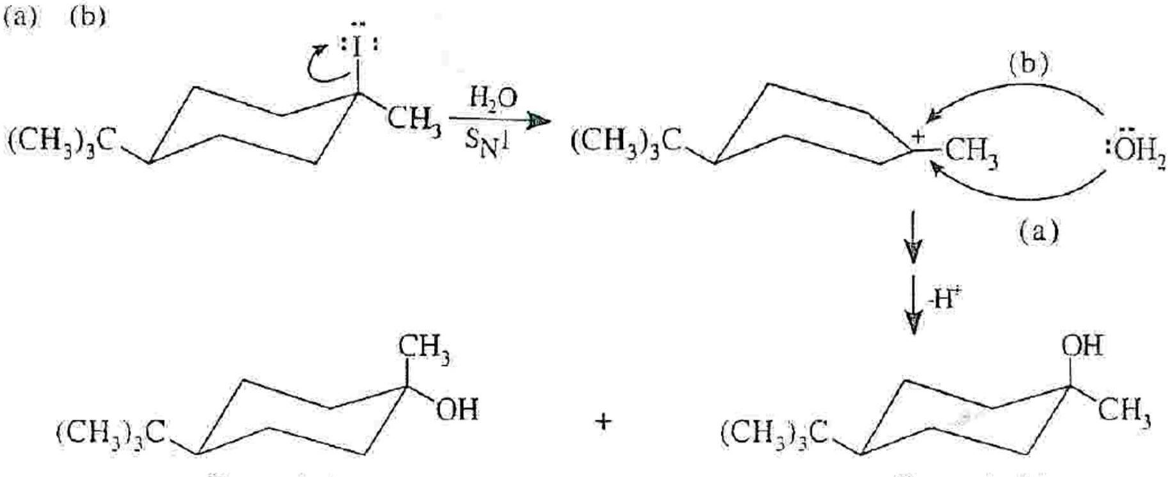
(*R*)-(-)-2-Iodobutane

(+)-2-Iodobutane has the (*S*) configuration

Problem 6.4 ➤ Karbokatyonların üçgen düzlem yapıya sahip olduğunu aklınızda tutarak, aşağıdaki tepkimeden beklediğiniz (a) karbokatyon ara ürünü için bir yapı, ve (b) alkol (veya alkollerin) yapılarını yazınız.



6.4 (a) (b)

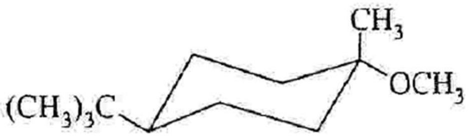


By path (a)

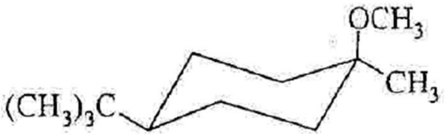
By path (b)

Problem 6.4'te reaktant olarak verilen sikloheksan türevlerinin metanolizinden hangi ürünü (veya ürünleri) beklersiniz? ◀ **Problem 6.5**

6.5



and



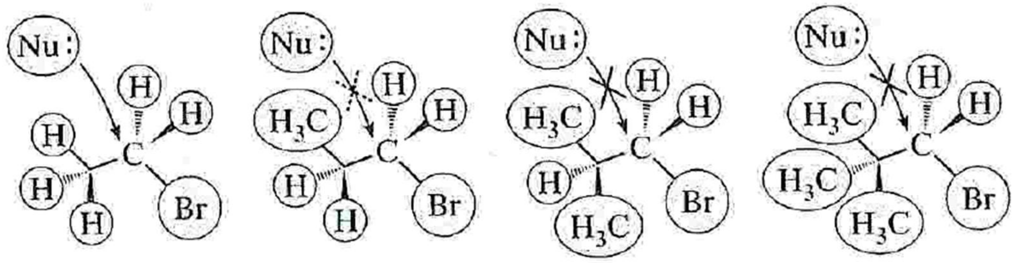
Problem 6.6 ➤ Birincil alkil halojenürlerin bağıl etanoliz hızları aşağıdaki gibidir: CH_3CH_2Br, 1,0; $CH_3CH_2CH_2Br$, 0,28; $(CH_3)_2CHCH_2Br$, 0,030; $(CH_3)_3CCH_2Br$, 0,00000042

(a) Bu tepkimelerin her biri, muhtemelen S_N1 mi yoksa S_N2 mi olmalıdır?

(b) Gözlenen bağıl etkinlikleri nasıl açıklarsınız?

6.6 (a) Being primary halides, the reactions are most likely to be S_N2, with the nucleophile in each instance being a molecule of the solvent (i.e., a molecule of ethanol).

(b) Steric hindrance is provided by the substituent or substituents on the carbon β to the carbon bearing the leaving group. With each addition of a methyl group at the β carbon (below), the number of pathways open to the attacking nucleophile becomes fewer.



Aşağıdaki çözücüleri, protik ya da aprotik olarak sınıflandırınız. ◄ **Problem 6.7**

Formik asit, $H\overset{\overset{O}{\|}}{C}OH$; aseton, $CH_3\overset{\overset{O}{\|}}{C}CH_3$; asetonitril, $CH_3C{\equiv}N$; formamit, $H\overset{\overset{O}{\|}}{C}NH_2$; kükürt dioksit, SO_2; amonyak, NH_3; trimetilamin, $N(CH_3)_3$; etilen glikol, $HOCH_2CH_2OH$.

6.7 **Protic solvents** are those that have an H bonded to an oxygen or nitrogen (or to another strongly electronegative atom). Therefore, the protic solvents are formic acid, $H\overset{\overset{O}{\|}}{C}OH$; formamide, $H\overset{\overset{O}{\|}}{C}NH_2$; ammonia, NH_3; and ethylene glycol, $HOCH_2CH_2OH$

Aprotic solvents lack an H bonded to a strongly electronegative element. Aprotic solvents in this list are acetone, $CH_3\overset{\overset{O}{\|}}{C}CH_3$; acetonitrile, $CH_3C{\equiv}N$; sulfur dioxide, SO_2; and trimethylamine, $N(CH_3)_3$.

Propil bromürün sodyum siyanürle (NaCN) tepkimesinin, DMF içinde mi, yoksa etanol içinde mi daha hızlı olmasını beklersiniz? ◄ **Problem 6.8**

$$CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$$

6.8 The reaction is an S_N2 reaction. In the polar aprotic solvent (DMF), the nucleophile (CN^-) will be relatively unencumbered by solvent molecules, and, therefore, it will be more reactive than in ethanol. As a result, the reaction will occur faster in *N,N*-dimethylformamide.

Bir protik çözücü içerisinde aşağıdakilerden hangisinin daha güçlü nükleofil olmasını beklersiniz? ◄ **Problem 6.9**

(a) $CH_3CO_2^-$ veya CH_3O^-? (b) H_2O veya H_2S? (c) $(CH_3)_3P$ veya $(CH_3)_3N$?

6.9 (a) CH_3O^-

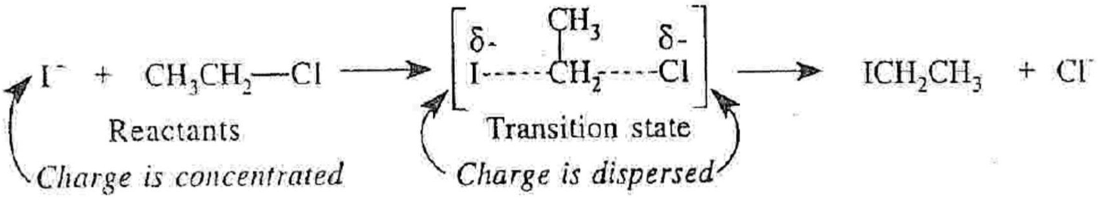
(b) H_2S

(c) $(CH_3)_3P$

Problem 6.10 ➤ *ter*-Bütil bromür, metanol ve su karışımı içinde solvolize maruz bırakıldığında, (karışımdaki bromür iyonlarından hesaplanan) solvoliz hızı, karışım içindeki su yüzdesi artırıldığında *artmaktadır*. (a) Bu olayı açıklayınız. (b) Karışımdaki su yüzdesi arttığında, etil klorür ve potasyum iyodürün metanol-su karışımı içerisinde verdiği S_N2 tepkimesinin hızı *azalmaktadır*, bu gözlemi açıklayınız.

6.10 (a) Increasing the percentage of water in the mixture increases the polarity of the solvent. (Water is more polar than methanol.) Increasing the polarity of the solvent increases the rate of the solvolysis because separated charges develop in the transition state. The more polar the solvent, the more the transition state is stabilized (Section 6.14D).

(b) In an S_N2 reaction of this type, the charge becomes dispersed in the transition state:



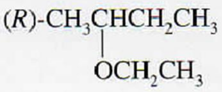
Increasing the polarity of the solvent increases the stabilization of the reactant I^- more than the stabilization of the transition state, and thereby increases the free energy of activation, thus decreasing the rate of reaction.

Problem 6.11 ➤ Aşağıdaki bileşiklerin metanol içerisinde CH_3O^- ile yapılan S_N2 tepkimelerindeki etkinlik sırasını, azalma yönünde yazınız. CH_3OH: CH_3F, CH_3Cl, CH_3Br, CH_3I, $CH_3OSO_2CF_3$, $^{14}CH_3OH$.

6.11 $CH_3OSO_2CF_3 > CH_3I > CH_3Br > CH_3Cl > CH_3F > {}^{14}CH_3OH$

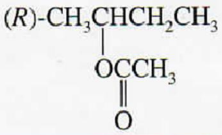
(Most reactive) (Least reactive)

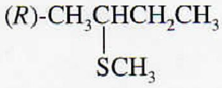
Problem 6.12 ➤ (*S*)-2-Bromobütandan başlayarak, aşağıdaki bileşiklerin her birinin sentezini plânlayınız.

(a)

(*R*)-$CH_3\underset{\underset{OCH_2CH_3}{|}}{C}HCH_2CH_3$

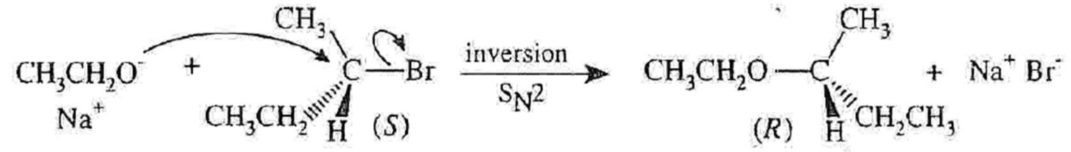
(c)

(*R*)-$CH_3\underset{\underset{SH}{|}}{C}HCH_2CH_3$

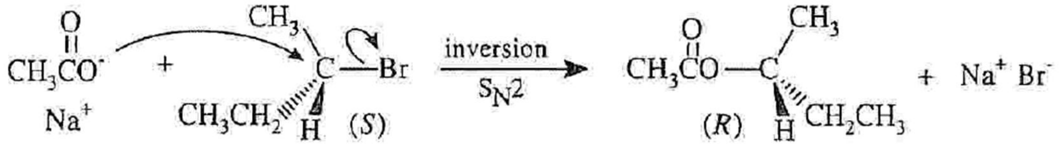
(b)

(*R*)-$CH_3\underset{\underset{\underset{\underset{O}{\|}}{OCCH_3}}{|}}{C}HCH_2CH_3$

(d)

(*R*)-$CH_3\underset{\underset{SCH_3}{|}}{C}HCH_2CH_3$

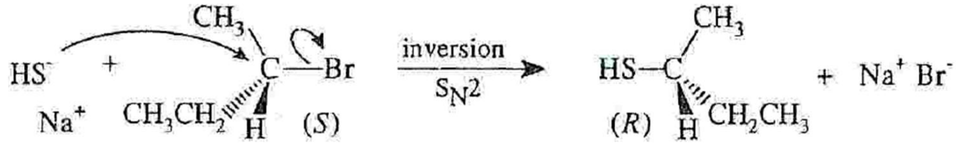
6.12 (a)



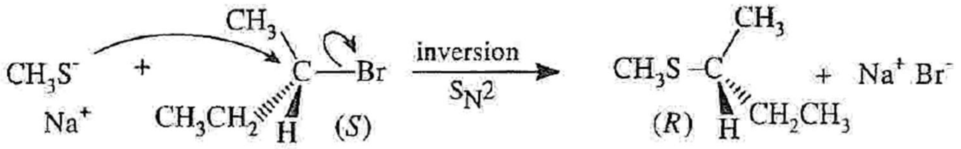
(b)



(c)



(d)



6.13 Propil bromürün nükleofilik yer değiştirme tepkimesini kullanarak aşağıdaki bileşiklerin her birini nasıl sentezleyebileceğinizi gösteriniz. (İstediğiniz bileşikleri kullanabilirsiniz)

(a) $CH_3CH_2CH_2OH$

(b) $CH_3CH_2CH_2I$

(c) $CH_3CH_2OCH_2CH_2CH_3$

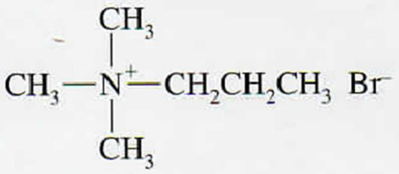
(d) $CH_3CH_2CH_2—S—CH_3$

(e)

$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_3$

(f) $CH_3CH_2CH_2N_3$

(g)



$CH_3—\underset{CH_3}{\overset{CH_3}{N^+}}—CH_2CH_2CH_3\ Br^-$

(h) $CH_3CH_2CH_2CN$

(i) $CH_3CH_2CH_2SH$

6.13 (a) $CH_3CH_2CH_2Br + NaOH \longrightarrow CH_3CH_2CH_2OH + NaBr$

(b) $CH_3CH_2CH_2Br + NaI \longrightarrow CH_3CH_2CH_2I + NaBr$

(c) $CH_3CH_2CH_2Br + CH_3CH_2ONa \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + NaBr$

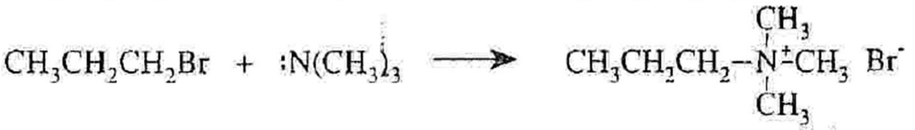
(d) $CH_3CH_2CH_2Br + CH_3SNa \longrightarrow CH_3CH_2CH_2SCH_3 + NaBr$

(e)

$CH_3CH_2CH_2Br + CH_3\overset{O}{\overset{\|}{C}}-ONa \longrightarrow CH_3CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3 + NaBr$

(f) $CH_3CH_2CH_2Br + NaN_3 \longrightarrow CH_3CH_2CH_2N_3 + NaBr$

(g)



$CH_3CH_2CH_2Br + :N(CH_3)_3 \longrightarrow CH_3CH_2CH_2-\underset{CH_3}{\overset{CH_3}{N^{\pm}}}CH_3\ Br^-$

(h) $CH_3CH_2CH_2Br + NaCN \longrightarrow CH_3CH_2CH_2CN + NaBr$

(i) $CH_3CH_2CH_2Br + NaSH \longrightarrow CH_3CH_2CH_2SH + NaBr$

6.14 S_N2 Mekanizması ile hangi halojenürün daha hızlı tepkime vereceğini beklersiniz? Cevabınızı açıklayınız.

(a) $CH_3CH_2CH_2Br$ veya $(CH_3)_2CHBr$
(b) $CH_3CH_2CH_2CH_2Cl$ veya $CH_3CH_2CH_2CH_2I$
(c) $(CH_3)_2CHCH_2Cl$ veya $CH_3CH_2CH_2CH_2Cl$
(d) $(CH_3)_2CHCH_2CH_2Cl$ veya $CH_3CH_2CH(CH_3)CH_2Cl$
(e) C_6H_5Br veya $CH_3CH_2CH_2CH_2CH_2CH_2Cl$

6.14 (a) 1-Bromopropane would react more rapidly because, being a primary halide, it is less hindered.

(b) 1-Iodobutane, because iodide ion is a better leaving group than chloride ion.

(c) 1-Chlorobutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylpropane.

(d) 1-Chloro-3-methylbutane, because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methylbutane.

(e) 1-Chlorohexane because it is a primary halide. Phenyl halides are unreactive in S_N2 reactions.

6.15 Protik bir çözücü içerisinde her bir tepkime çiftinden hangisi daha hızlı S_N2 tepkimesi verir?

(a) (1) $CH_3CH_2CH_2Cl + CH_3CH_2O^- \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + Cl^-$
ya da
(2) $CH_3CH_2CH_2Cl + CH_3CH_2OH \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + HCl$

(b) (1) $CH_3CH_2CH_2Cl + CH_3CH_2O^- \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + Cl^-$
ya da
(2) $CH_3CH_2CH_2Cl + CH_3CH_2S^- \longrightarrow CH_3CH_2CH_2SCH_2CH_3 + Cl^-$

(c) (1) $CH_3CH_2CH_2Br + (C_6H_5)_3N \longrightarrow CH_3CH_2CH_2N(C_6H_5)_3^+ + Br^-$
ya da
(2) $CH_3CH_2CH_2Br + (C_6H_5)_3P \longrightarrow CH_3CH_2CH_2P(C_6H_5)_3^+ + Br^-$

(d) (1) $CH_3CH_2CH_2Br\ (1{,}0M) + CH_3O^-\ (1{,}0M) \longrightarrow CH_3CH_2CH_2OCH_3 + Br^-$
ya da
(2) $CH_3CH_2CH_2Br\ (1{,}0M) + CH_3O^-\ (2{,}0M) \longrightarrow CH_3CH_2CH_2OCH_3 + Br^-$

6.15 (a) Reaction (1) because ethoxide ion is a stronger nucleophile than ethanol.

(b) Reaction (2) because the ethyl sulfide ion is a stronger nucleophile than the ethoxide ion in a protic solvent. (Because sulfur is larger than oxygen, the ethyl sulfide ion is less solvated and it is more polarizable.)

(c) Reaction (2) because triphenylphosphine $[(C_6H_5)_3P]$ is a stronger nucleophile than triphenylamine. (Phosphorus atoms are larger than nitrogen atoms.)

(d) Reaction (2) because in an S_N2 reaction the rate depends on the concentration of the substrate and the nucleophile. In reaction (2) the concentration of the nucleophile is twice that of the reaction (1).

6.16 Aşağıdaki her bir tepkime çiftinden hangisi daha hızlı S_N1 tepkimesi verir? Cevabınızı açıklayınız.

(a) (1) $(CH_3)_3CCl + H_2O \longrightarrow (CH_3)_3COH + HCl$
ya da
(2) $(CH_3)_3CBr + H_2O \longrightarrow (CH_3)_3COH + HBr$

(b) (1) $(CH_3)_3CCl + H_2O \longrightarrow (CH_3)_3COH + HCl$
ya da
(2) $(CH_3)_3CCl + CH_3OH \longrightarrow (CH_3)_3COCH_3 + HCl$

(c) (1) $(CH_3)_3CCl\ (1{,}0M) + CH_3CH_2O^-\ (1{,}0M) \xrightarrow{EtOH} (CH_3)_3COCH_2CH_3 + Cl^-$
ya da
(2) $(CH_3)_3CCl\ (2{,}0M) + CH_3CH_2O^-\ (1{,}0M) \xrightarrow{EtOH} (CH_3)_3COCH_2CH_3 + Cl^-$

(d) (1) $(CH_3)_3CCl\ (1{,}0M) + CH_3CH_2O^-\ (1{,}0M) \xrightarrow{EtOH} (CH_3)_3COCH_2CH_3 + Cl^-$
ya da
(2) $(CH_3)_3CCl\ (1{,}0M) + CH_3CH_2O^-\ (2{,}0M) \xrightarrow{EtOH} (CH_3)_3COCH_2CH_3 + Cl^-$

(e) (1) $(CH_3)_3CCl + H_2O \longrightarrow (CH_3)_3COH + HCl$
ya da
(2) $C_6H_5Cl + H_2O \longrightarrow C_6H_5OH + HCl$

6.16 (a) Reaction (2) because bromide ion is a better leaving group than chloride ion.

(b) Reaction (1) because water is a more polar solvent than methanol, and S_N1 reactions take place faster in more polar solvents.

(c) Reaction (2) because the concentration of the substrate is twice that of reaction (1). (The major reaction would be E2. However, the problem asks us to consider that small portion of the overall reaction that proceeds by an S_N1 pathway.)

(d) Both reactions would take place at the same rate because, being S_N1 reactions, they are independent of the concentration of the nucleophile.
(The major reaction would be E2. However, the problem asks us to consider that small portion of the overall reaction that proceeds by an S_N1 pathway.)

(e) Reaction (1) because the substrate is a tertiary halide. Phenyl halides are unreactive in S_N1 reactions.

6.17 Çıkış maddesi olarak metil, etil veya siklopentil halojenürler, gerekli çözücüler ve inorganik maddeleri kullanarak aşağıdakilerin her birinin sentezini tasarlayınız. Bir basamaktan daha fazlası gerekli olabilir, fakat problemin daha önceki şıklarında yaptıklarınızı yeniden tekrar etmeyiniz.

(a) CH_3I
(b) CH_3CH_2I
(c) CH_3OH
(d) CH_3CH_2OH
(e) CH_3SH
(f) CH_3CH_2SH
(g) CH_3CN
(h) CH_3CH_2CN
(i) CH_3OCH_3
(j) $CH_3OCH_2CH_3$
(k) Siklopenten

6.17 Possible methods are given here.

(a) $CH_3Cl \xrightarrow[CH_3OH \\ S_N2]{I^-} CH_3I$

(b) $CH_3CH_2Cl \xrightarrow[CH_3OH \\ S_N2]{I^-} CH_3CH_2I$

(c) $CH_3Cl \xrightarrow[CH_3OH/H_2O \\ S_N2]{OH^-} CH_3OH$

(d) $CH_3CH_2Cl \xrightarrow[CH_3OH/H_2O \\ S_N2]{OH^-} CH_3CH_2OH$

(e) $CH_3Cl \xrightarrow[CH_3OH \\ S_N2]{SH^-} CH_3SH$

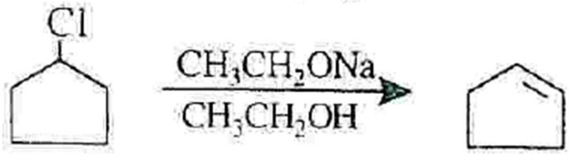
(f) $CH_3CH_2Cl \xrightarrow[CH_3OH \\ S_N2]{SH^-} CH_3CH_2SH$

(g) $CH_3Cl \xrightarrow[DMF]{CN^-} CH_3CN$

(h) $CH_3CH_2Cl \xrightarrow[DMF]{CN^-} CH_3CH_2CN$

(i) $CH_3OH \xrightarrow[(-H_2)]{NaH} CH_3ONa \xrightarrow[CH_3OH]{CH_3I} CH_3OCH_3$

(j) $CH_3CH_2OH \xrightarrow[(-H_2)]{NaH} CH_3CH_2ONa \xrightarrow{CH_3I} CH_3CH_2OCH_3$

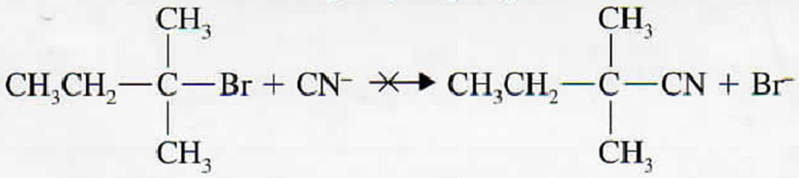
(k)


6.18 Aşağıda varsayımsal bazı nükleofilik yer değiştirme tepkimelerini görüyorsunuz. Belirtilen ürünler uygun bir hızda oluşmadığından, bunların hiç biri sentetik olarak yararlı değildir. Her bir durumda, tepkimenin gösterildiği şekilde gerçekleşmemesinin nedenlerini açıklayınız.

(a) $CH_3CH_2CH_3 + OH^- \not\rightarrow CH_3CH_2OH + CH_3^-$

(b) $CH_3CH_2CH_3 + OH^- \not\rightarrow CH_3CH_2CH_2OH + H^-$

(c) □ $+ OH^- \not\rightarrow {}^-CH_2CH_2CH_2CH_2OH$

(d)


$CH_3CH_2-C(CH_3)_2-Br + CN^- \not\rightarrow CH_3CH_2-C(CH_3)_2-CN + Br^-$

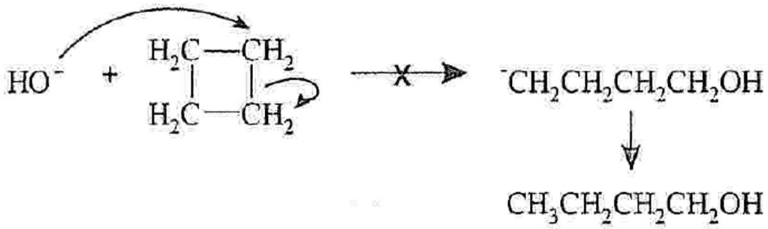
(e) $NH_3 + CH_3OCH_3 \not\rightarrow CH_3NH_2 + CH_3OH$

(f) $NH_3 + CH_3OH_2^+ \not\rightarrow CH_3NH_3^+ + H_2O$

6.18 (a) The reaction will not take place because the leaving group would have to be a methyl anion, a very powerful base, and a very poor leaving group.

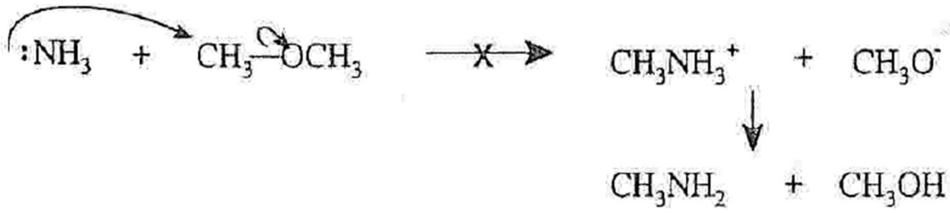
(b) The reaction will not take place because the leaving group would have to be a hydride ion, a very powerful base, and a very poor leaving group.

(c) The reaction will not take place because the leaving group would have to be a carbanion, a very powerful base, and a very poor leaving group.



(d) The reaction will not take place by an S_N2 mechanism because the substrate is a tertiary halide, and is, therefore, not susceptible to S_N2 attack because of the steric hindrance. (A very small amount of S_N1 reaction may take place, but the main reaction will be E2 to produce an alkene.)

(e) The reaction will not take place because the leaving group would have to be a CH_3O^- ion, a strong base, and a very poor leaving group.



(f) The reaction will not take place because the first reaction that would take place would be an acid-base reaction that would convert the ammonia to an ammonium ion. An ammonium ion, because it lacks an electron pair, is not nucleophilic.

$$NH_3 + CH_3\overset{+}{O}H_2 \rightleftharpoons NH_4^+ + CH_3OH$$

6.19 Etanol içerisinde KOH kullanılarak yapılan dehidrohalojenleme ile hem 1-bromo-2-feniletandan hem de 1-bromo-1-feniletandan stiren ($C_6H_5CH{=}CH_2$) hazırlamanız istenseydi daha iyi bir alken verimi için çıkış maddesi olarak hangi halojenürü seçerdiniz? Cevabınızı açıklayınız.

6.19 The better yield will be obtained by using the secondary halide, 1-bromo-1-phenylethane, because the desired reaction is E2. Using the primary halide will result in substantial S_N2 reaction as well, producing the alcohol instead of the desired alkene.

6.20 Göreviniz, aşağıdaki tepkimelerden birini kullanarak izopropil metil eter [$CH_3OCH(CH_3)_2$] hazırlamak olsun. Hangi tepkime daha iyi verimle yürüyecektir? Seçiminizin nedenini açıklayınız.

(1) $CH_3ONa + (CH_3)_2CHI \longrightarrow CH_3OCH(CH_3)_2$
(2) $(CH_3)_2CHONa + CH_3I \longrightarrow CH_3OCH(CH_3)_2$

6.20 Reaction (2) would give the better yield because the desired reaction is an S_N2 reaction, and the substrate is a methyl halide. Use of reaction (1) would, because the substrate is a secondary halide, result in considerable elimination by an E2 pathway.

6.21 Aşağıdaki tepkimelerin her birinden hangi ürün veya ürünlerin oluşmasını beklersiniz? Her bir şıkta ürünün hangi mekanizma ile (S_N1, S_N2, E1 ya da E2) oluşacağını belirtiniz ve her bir ürünün bağıl miktarını tahmin ediniz (yani, tek ürün, ana ürü, yan ürün, vb.)

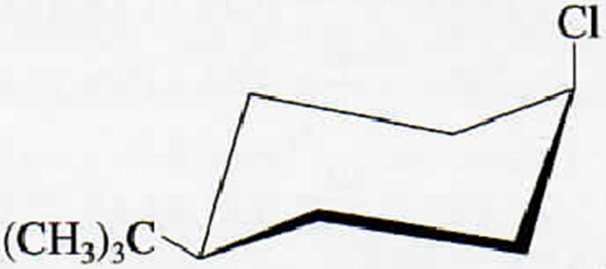
(a) $CH_3CH_2CH_2CH_2CH_2Br + CH_3CH_2O^- \xrightarrow[CH_3CH_2OH]{50°C}$

(b) $CH_3CH_2CH_2CH_2CH_2Br + (CH_3)_3CO^- \xrightarrow[(CH_3)_3COH]{50°C}$

(c) $(CH_3)_3CBr + CH_3O^- \xrightarrow[CH_3OH]{50°C}$

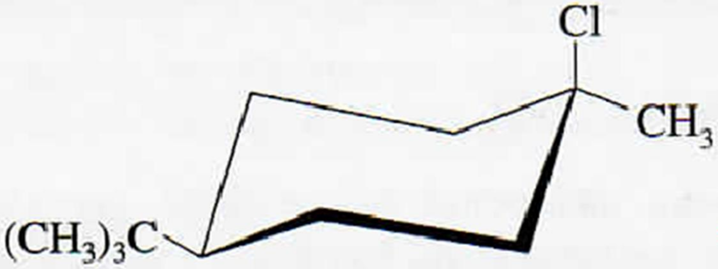
(d) $(CH_3)_3CBr + (CH_3)_3CO^- \xrightarrow[(CH_3)_3COH]{50°C}$

(e)



$+ I^- \xrightarrow[\text{aseton}]{50°C}$

(f)



$\xrightarrow[CH_3OH]{25°C}$

(g) 3-Kloropentan $+ CH_3O^- \xrightarrow[CH_3OH]{50°C}$

(h) 3-Kloropentan $+ CH_3CO_2^- \xrightarrow[CH_3CO_2H]{50°C}$

(i) $HO^- +$ (*R*)-2-bromobütan $\xrightarrow{25°C}$

(j) (*S*)-3-Bromo-3-metilheksan $\xrightarrow[CH_3OH]{25°C}$

(k) (*S*)-2-Bromooktan $+ I^- \xrightarrow[CH_3OH]{50°C}$

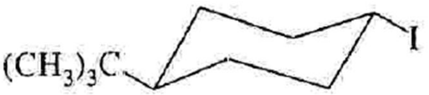
6.21 (a) The major product would be $CH_3CH_2CH_2CH_2CH_2OCH_2CH_3$ (by an S_N2 mechanism) because the substrate is primary and the nucleophile-base is not hindered. Some $CH_3CH_2CH_2CH{=}CH_2$ would be produced by an E2 mechanism.

(b) The major product would be $CH_3CH_2CH_2CH{=}CH_2$ (by an E2 mechanism), even though the substrate is primary because the base is a hindered strong base. Some $CH_3CH_2CH_2CH_2CH_2OC(CH_3)_3$ would be produced by an S_N2 mechanism.

(c) For all practical purposes, $(CH_3)_2C{=}CH_2$ (by an E2 mechanism) would be the only product because the substrate is tertiary and the base is strong.

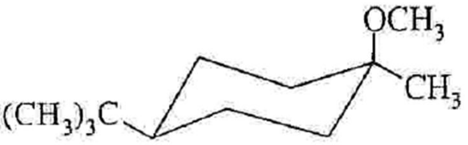
(d) Same answer as (c) above.

(e)



(formed by an S_N2 mechanism) would, for all practical purposes, be the only product. Iodide ion is a very weak base and a good nucleophile.

(f) Because the substrate is tertiary and the only nucleophile is the solvent, mechanism is S_N1. The two products that follow would be formed.



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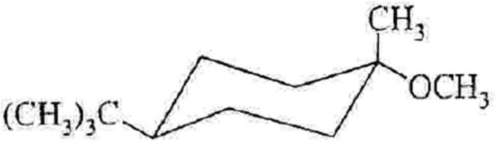
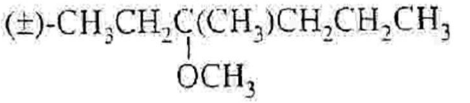


(g) $CH_3CH{=}CHCH_2CH_3$ (by an E2 mechanism) would be the major product because the substrate is secondary and the base/nucleophile is a strong base. Some of the ether, $CH_3CH_2CH(OCH_3)CH_2CH_3$, would be formed by an S_N2 pathway.

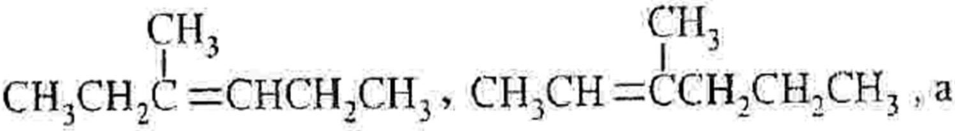
(h) The major product would be $CH_3CH_2CH(O_2CCH_3)CH_2CH_3$ (by an S_N2 mechanism) because the acetate ion is a weak base. Some $CH_3CH{=}CHCH_2CH_2CH_3$ might be formed by an E2 pathway.

(i) $CH_3CH{=}CHCH_3$ and $CH_2{=}CHCH_2CH_3$ (by E2) would be major products, and (*S*)-$CH_3CH(OH)CH_2CH_3$ (by S_N2) would be the minor product.

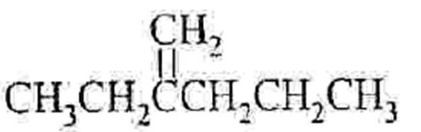
(j)



$(\pm)\text{-}CH_3CH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}(CH_3)CH_2CH_2CH_3$ (by S_N1) would be the major product.



$CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2CH_3$, $CH_3CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH_2CH_2CH_3$, and

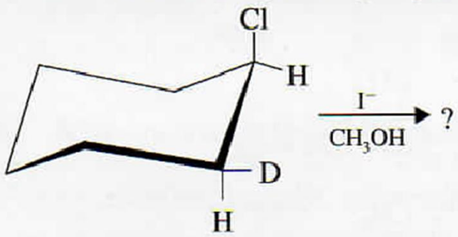


$CH_3CH_2\overset{\displaystyle CH_2}{\overset{\|}{C}}CH_2CH_2CH_3$ (by E1) would be minor products.

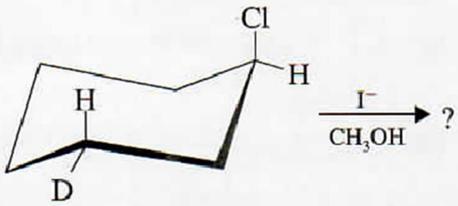
(k) (*R*)-$CH_3CHIC_6H_{13}$ (by S_N2) would be the only product.

6.22 Aşağıdaki döteryumla etiketlenmiş bileşiklerin yer değiştirme ürünlerinin yapılarını konformasyonlarıyla gösteriniz.

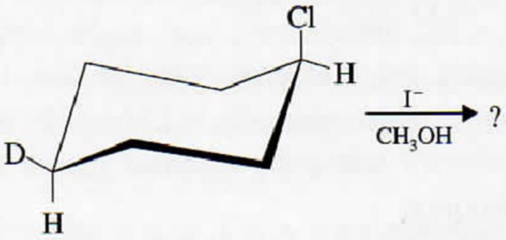
(a)



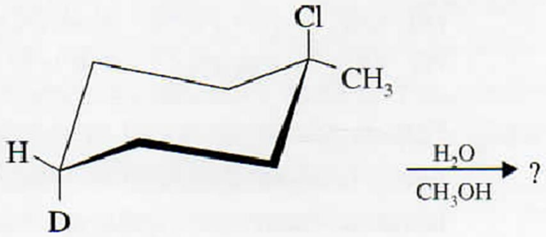
(c)



(b)

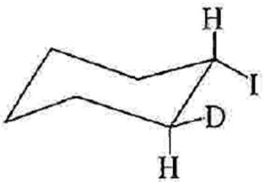


(d)

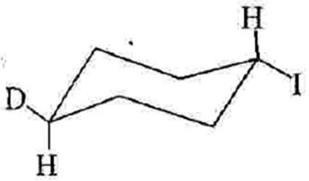


6.22 (a), (b), and (c) are all S_N2 reactions and, therefore, proceed with inversion of configuration. The products are

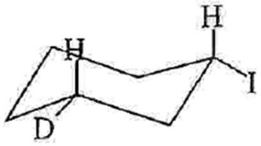
(a)



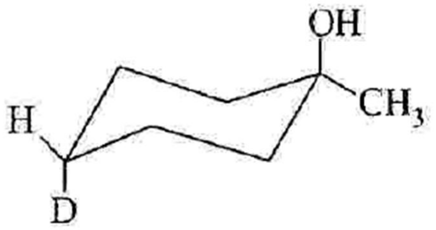
(b)



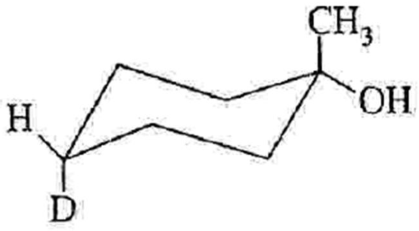
(c)

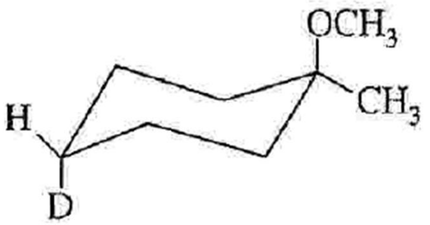


(d) is an S_N1 reaction. The carbocation that forms can react with either nucleophile (H_2O or CH_3OH) from either the top or bottom side of the molecule. Four substitution products (below) would be obtained. (Considerable elimination by an E1 path would also occur.)



and





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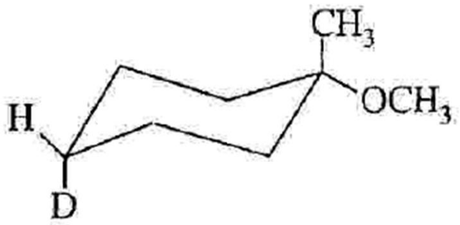
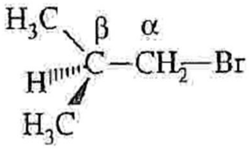
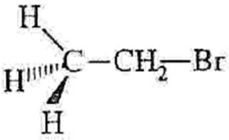


6.23 Etil bromür ve izobütil bromürün her ikisi de birincil halojenür olmasına rağmen, etil bromür, izobütil bromürden 10 kat daha hızlı S_N2 tepkimesi verir. Her bir bileşik güçlü bir baz/nükleofil ($CH_3CH_2O^-$) ile etkileştirildiğinde, izobütil bromür, etil bromürün tam aksine, yer değiştirme ürününden daha çok ayrılma ürünü verir. Bu sonucu nasıl açıklarsınız?

6.23 Isobutyl bromide is more sterically hindered than ethyl bromide because of the methyl groups on the β carbon atom.



Isobutyl bromide



Ethyl bromide

This steric hindrance causes isobutyl bromide to react more slowly in S_N2 reactions and to give relatively more elimination (by an E2 path) when a strong base is used.

6.24 I^- iyonunun CH_3CH_2Cl ile olan tepkimesini göz önüne alınız. **(a)** Tepkimenin S_N1 mi yoksa S_N2 mekanizmasıyla mı gerçekleşmesini beklersiniz? 60°C'da tepkime hız sabiti, 5×10^{-5} L mol^{-1} s^{-1}'dir. **(b)** $[I^-] = 0,1$ mol L^{-1} ve $[CH_3CH_2Cl] = 0,1$ mol L^{-1} ise tepkime hızı nedir? **(c)** Eğer $[I^-] = 0,1$ mol L^{-1} ve $[CH_3CH_2Cl] = 0,2$ mol L^{-1} ise tepkime hızı nedir? **(d)** $[I^-] = 0,2$ mol L^{-1} ve $[CH_3CH_2Cl] = 0,1$ mol L^{-1} ise tepkime hızı nedir? **(e)** $[I^-] = 0,2$ mol L^{-1} ve $[CH_3CH_2Cl] = 0,2$ mol L^{-1} ise tepkime hızı nedir?

6.24 (a) S_N2 because the substrate is a 1° halide.

(b) $\text{Rate} = k\,[CH_3CH_2Cl][I^-]$

$$= 5 \times 10^{-5}\ \text{L mol}^{-1}\text{s}^{-1} \times 0.1\ \text{mol L}^{-1} \times 0.1\ \text{mol L}^{-1}$$

$$\text{Rate} = 5 \times 10^{-7}\ \text{mol L}^{-1}\text{s}^{-1}$$

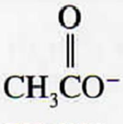
(c) 1×10^{-6} mol $L^{-1}s^{-1}$

(d) 1×10^{-6} mol $L^{-1}s^{-1}$

(e) 2×10^{-6} mol $L^{-1}s^{-1}$

6.25 Aşağıdaki protik bir çözücü içerisinde reaktif çiftlerinden hangisi daha güçlü nükleofilik özellik gösterir?

(a) CH_3NH^- ya da CH_3NH_2

(b) CH_3O^- ya da  $CH_3C(=O)O^-$

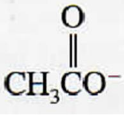
(c) CH_3SH ya da CH_3OH

(d) $(C_6H_5)_3N$ ya da $(C_6H_5)_3P$

(e) H_2O ya da H_3O^+

(f) NH_3 ya da NH_4^+

(g) H_2S ya da HS^-

(h)  $CH_3C(=O)O^-$ ya da OH^-

6.25 (a) CH_3NH^- because it is the stronger base.

(b) CH_3O^- because it is the stronger base.

(c) CH_3SH because sulfur atoms are larger and more polarizable than oxygen atoms.

(d) $(C_6H_5)_3P$ because phosphorus atoms are larger and more polarizable than nitrogen atoms.

(e) H_2O because it is the stronger base.

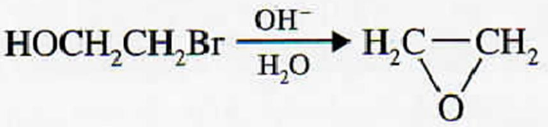
(f) NH_3 because it is the stronger base.

(g) HS^- because it is the stronger base.

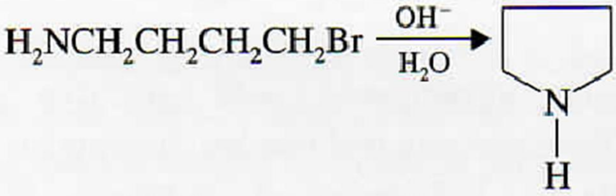
(h) OH^- because it is the stronger base.

6.26 Aşağıdaki tepkime ürünlerini açıklayıcı mekanizmaları yazınız.

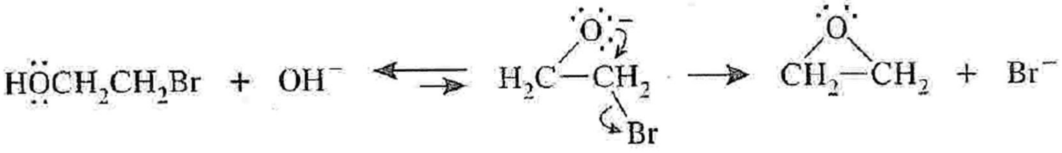
(a)



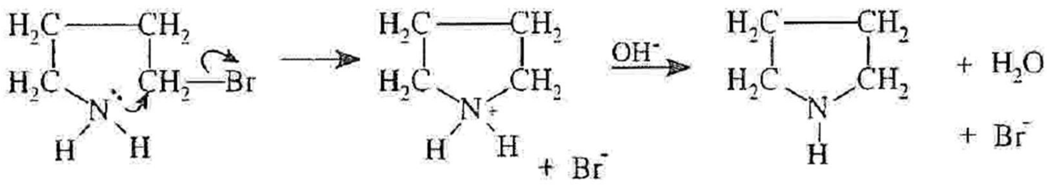
(b)



6.26 (a)

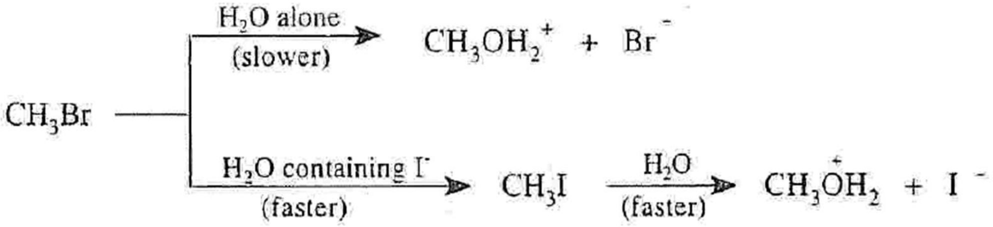


(b)



6.27 Alkil klorür ve alkil bromürlerin S_N2 tepkimelerinin çoğu, ortama sodyum iyodür veya potasyum iyodür katılmak suretiyle katalizlenir. Örneğin, metil bromürün hidrolizi, sodyum iyodür varlığında çok daha hızlı gerçekleşir. Bu sonucu nasıl açıklarsınız?

6.27 Iodide ion is a good nucleophile and a good leaving group; it can rapidly convert an alkyl chloride or alkyl bromide into an alkyl iodide, and the alkyl iodide can then react rapidly with another nucleophile. With methyl bromide in water, for example, the following reaction can take place:



$$CH_3Br \xrightarrow[\text{(slower)}]{H_2O\text{ alone}} CH_3OH_2^+ + Br^-$$

$$CH_3Br \xrightarrow[\text{(faster)}]{H_2O\text{ containing } I^-} CH_3I \xrightarrow[\text{(faster)}]{H_2O} CH_3\overset{+}{O}H_2 + I^-$$

6.28 Aşağıdaki gözlemleri açıklayınız: Metanol ve su karışımı içerisinde *ter*-bütil bromür, sodyum metoksitle etkileştirildiğinde, sodyum metoksit derişiminin artırılması, *ter*-bütil alkol ve *ter*-bütil metil eterin oluşum hızında farkedilir bir değişime yol açmaz. Fakat, sodyum metoksit derişiminin artırılması *ter*-bütil bromürün tükenme hızında belirgin bir değişikliğe neden olur.

6.28 *tert*-Butyl alcohol and *tert*-butyl methyl ether are formed via an S_N1 mechanism. The rate of the reaction is independent of the concentration of methoxide ion (from sodium methoxide). This, however, is only one reaction that causes *tert*-butyl bromide to disappear. A competing reaction that also causes *tert*-butyl bromide to disappear is an E2 reaction in which methoxide ion reacts with *tert*-butyl bromide. This reaction is dependent on the concentration of methoxide ion; therefore, increasing the methoxide ion concentration causes an increase in the rate of disappearance of *tert*-butyl bromide.

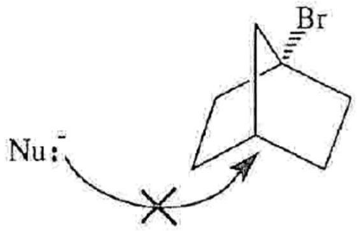
6.29 **(a)** *ter*-Bütil klorürün 2-metilpropene dönüşümünde olduğu gibi, genel olarak bir üçüncül alkil halojenürün alkene dönüşümündeki genel bir problemi göz önüne alınız. Ayrılmanın, yer değiştirmeden daha fazla olmasını sağlamak için hangi deneysel şartları seçersiniz? **(b)** Problemi tersinden, bir üçüncül alkil halojenürün yer değiştirmesini gerçekleştirmek olarak düşünün. Örnek olarak *ter*-bütil klorürün *ter*-bütil etere dönüşümünü kullanınız. Bu eteri, mümkün olan en yüksek verimde elde etmek için hangi deneysel şartları kullanırsınız?

6.29 (a) You should use a strong base, such as RO^-, at a higher temperature to bring about an E2 reaction.

(b) Here we want an S_N1 reaction. We use ethanol as the solvent *and as the nucleophile*, and we carry out the reaction at a low temperature so that elimination will be minimized.

6.30 1-Bromobisiklo[2.2.1]heptan, hem S_N2 hem de S_N1 tepkimelerine karşı son derece duyarsızdır. Bu davranışı açıklayınız.

6.30 1-Bromobicyclo[2.2.1]heptane is unreactive in an S_N2 reaction because it is a tertiary halide and its ring structure makes the backside of the carbon bearing the leaving group completely inaccessible to attack by a nucleophile.



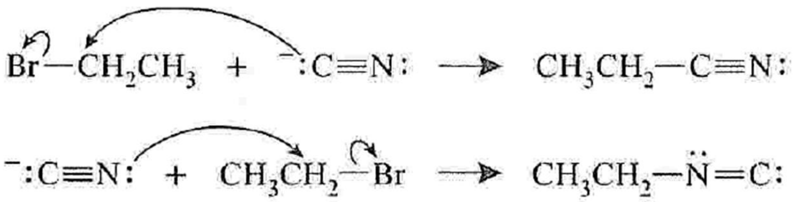
1-Bromobicyclo[2.2.1]heptane is unreactive in an S_N1 reaction because the ring structure makes it impossible for the carbocation that must be formed to assume the required trigonal planar geometry around the positively charged carbon. Any carbocation formed from 1-bromobicyclo[2.2.1]heptane would have a trigonal pyramidal arrangement of the $-CH_2-$ groups attached to the positively charged carbon (make a model). Such a structure does not allow stabilization of the carbocation by overlap of sp^3 orbitals from the alkyl groups (see Fig. 6.9).

6.31 Etil bromür, metanol içerisinde potasyum siyanür ile tepkime verdiğinde ana ürün CH_3CH_2CN'dir. Fakat, biraz da CH_3CH_2NC oluşur. Siyanür iyonu ve her iki ürün için Lewis yapılarını yazınız ve tepkimenin yürüyüşünün mekanistik açıklamasını yapınız.

6.31 The cyanide ion has two nucleophilic atoms; it is what is called an ambident nucleophile.

$$^{-}{:}C\equiv N{:}$$

It can react with a substrate using either atom, although the carbon atom is more nucleophilic.



$$Br{-}CH_2CH_3 + {}^{-}{:}C\equiv N{:} \longrightarrow CH_3CH_2{-}C\equiv N{:}$$

$$^{-}{:}C\equiv N{:} + CH_3CH_2{-}Br \longrightarrow CH_3CH_2{-}\ddot{N}{=}C{:}$$

6.32 Uygun alkil halojenürlerden başlayarak ve diğer gerekli reaktifleri kullanarak aşağıdaki her bir sentez için bir tasarım yapınız. Bir sentez için farklı ihtimaller olduğunda, en iyi verimi sağlayacak olanı şeçme hususunda dikkatli olmalısınız.

(a) Bütil *sek*-bütil eter

(b) $CH_3CH_2SC(CH_3)_3$

(c) Metil neopentil eter

(d) Metil fenil eter

(e) $C_6H_5CH_2CN$

(f) $CH_3CO_2CH_2C_6H_5$

(g) (*S*)-2-Pentanol

(h) (*R*)-2-İyodo-4-metilpentan

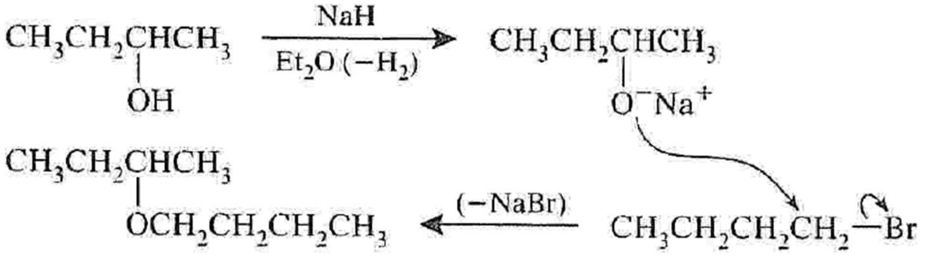
(i) $(CH_3)_3CCH{=}CH_2$

(j) *cis*-4-izopropilsikloheksanol

(k) (*R*)-$CH_3CH(CN)CH_2CH_3$

(l) *trans*-1-İyodo-4-metilsikloheksan

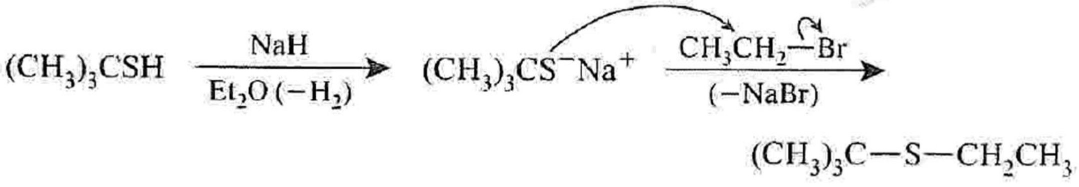
6.32 (a)



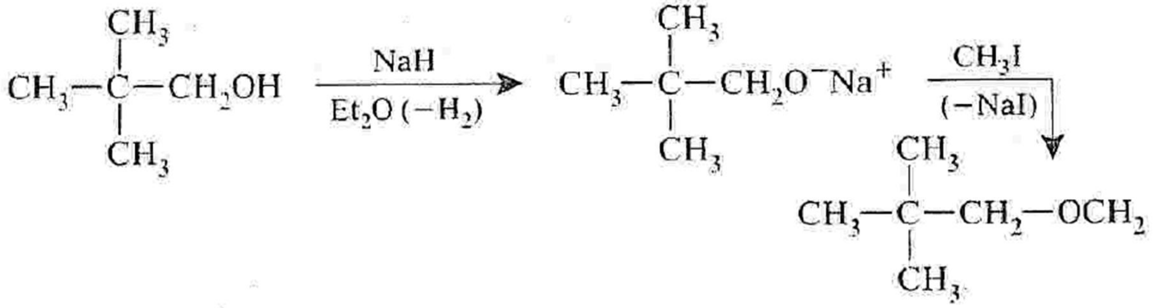
$$CH_3CH_2\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow[Et_2O\ (-H_2)]{NaH} CH_3CH_2\underset{O^-Na^+}{\underset{|}{C}}HCH_3$$

$$CH_3CH_2CH_2CH_2{-}Br \xrightarrow{(-NaBr)} CH_3CH_2\underset{OCH_2CH_2CH_2CH_3}{\underset{|}{C}}HCH_3$$

(b)

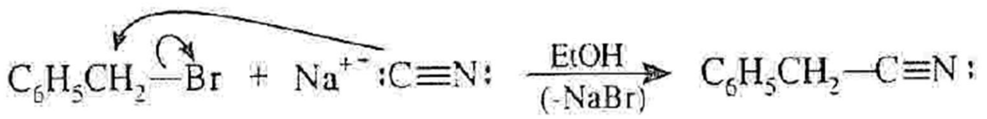


$$(CH_3)_3CSH \xrightarrow[Et_2O\ (-H_2)]{NaH} (CH_3)_3CS^-Na^+ \xrightarrow[(-NaBr)]{CH_3CH_2{-}Br} (CH_3)_3C{-}S{-}CH_2CH_3$$

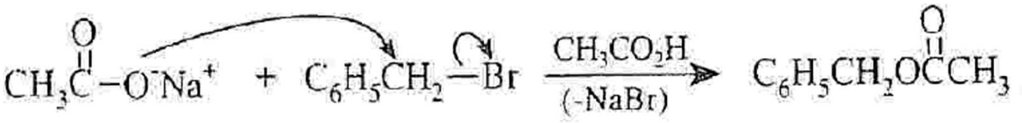
(c) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH \xrightarrow[Et_2O\,(-H_2)]{NaH} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2O^-Na^+ \xrightarrow[(-NaI)]{CH_3I} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-OCH_3$$

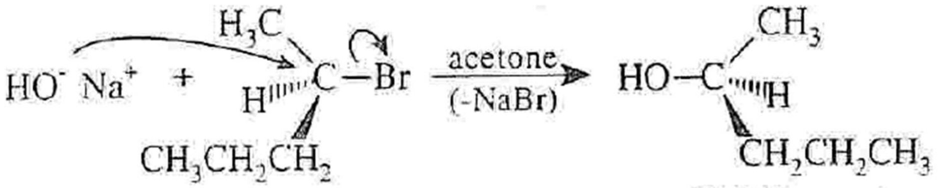
(d) $C_6H_5OH \xrightarrow[Et_2O\,(-H_2)]{NaH} C_6H_5O^-Na^+ \xrightarrow[(-NaI)]{CH_3I} C_6H_5OCH_3$

(e) 

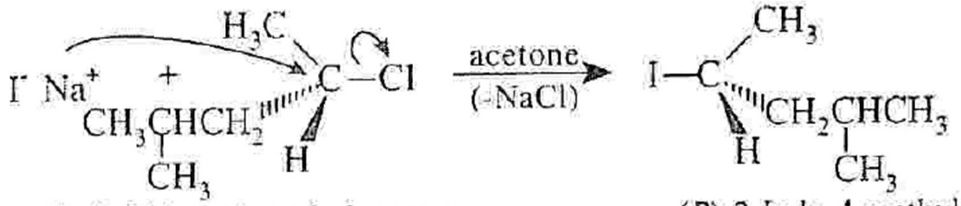
$$C_6H_5CH_2-Br + Na^{+-}:C\equiv N: \xrightarrow[(-NaBr)]{EtOH} C_6H_5CH_2-C\equiv N:$$

(f) 

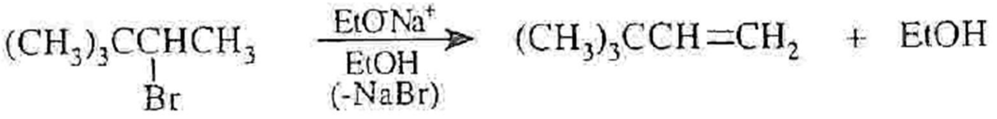
$$CH_3\overset{\overset{O}{\|}}{C}-O^-Na^+ + C_6H_5CH_2-Br \xrightarrow[(-NaBr)]{CH_3CO_2H} C_6H_5CH_2O\overset{\overset{O}{\|}}{C}CH_3$$

(g) 

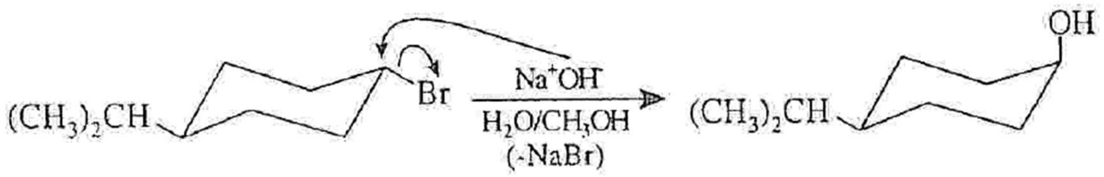
(*R*)-2-Bromopentane (*S*)-2-Pentanol

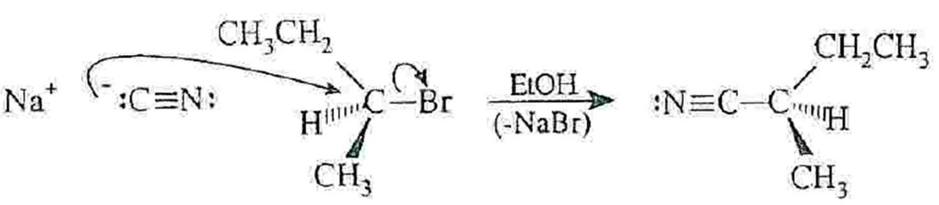
(h) 

(*S*)-2-Chloro-4-methylpentane (*R*)-2-Iodo-4-methylpentane

(i) 

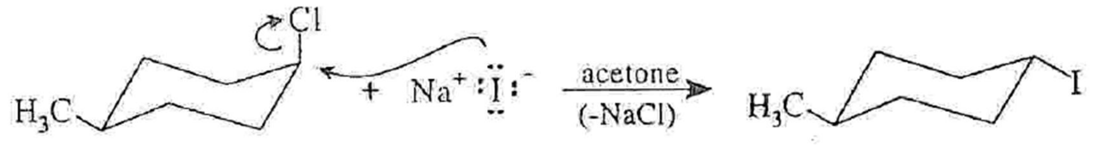
$$(CH_3)_3C\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow[\substack{EtOH\\(-NaBr)}]{EtO^-Na^+} (CH_3)_3CCH{=}CH_2 + EtOH$$

(j) 

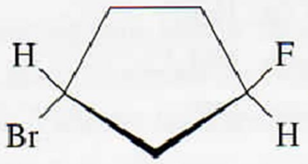
(k) 

(*S*)-2-Bromobutane

(I)



6.33 Aşağıdaki tepkimelerin her birinde oluşacak ürünlerin yapılarını yazınız.

(a) 

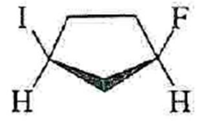
+ NaI (1 mol) $\xrightarrow[\text{aseton}]{}$ C_5H_8FI + NaBr

(b) 1,4-Dikloroheksan (1 mol) + NaI (1 mol) $\xrightarrow[\text{aseton}]{}$ $C_6H_{12}ClI$ + NaCl

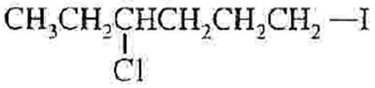
(c) 1,2-Dibromoetan (1 mol) + $NaSCH_2CH_2SNa \longrightarrow C_4H_8S_2$ + 2 NaBr

(d) 4-Kloro-1-bütanol + NaH $\xrightarrow[Et_2O]{(-H_2)}$ C_4H_8ClONa $\xrightarrow[Et_2O]{\text{ısı}}$ C_4H_8O + NaCl

(e) Propin + $NaNH_2$ $\xrightarrow[\text{sıvı } NH_3]{(-NH_3)}$ C_3H_3Na $\xrightarrow{CH_3I}$ C_4H_6 + NaI

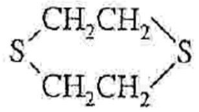
6.33 (a) 

(Formation of this product depends on the fact that bromide ion is a much better leaving group than fluoride ion.)

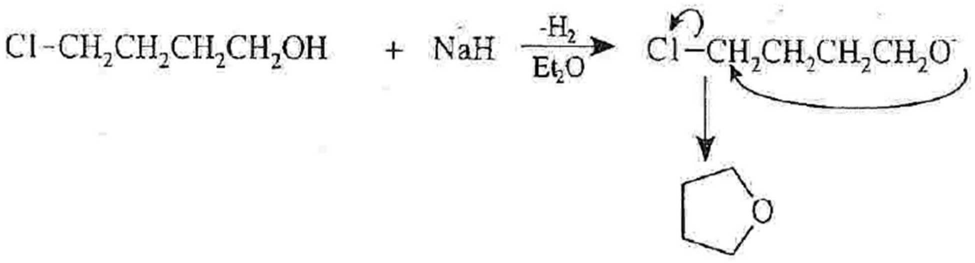
(b) 

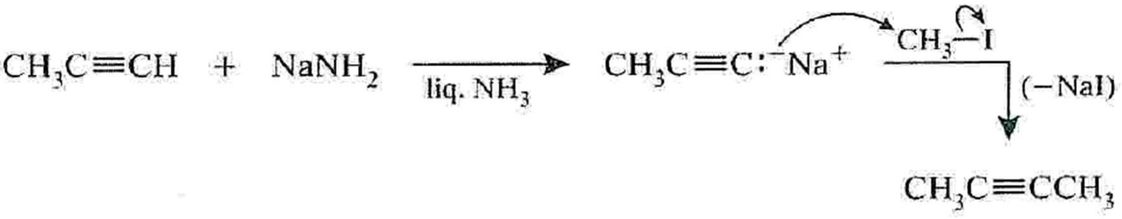
$CH_3CH_2\underset{\substack{|\\ Cl}}{C}HCH_2CH_2CH_2{-}I$

(Formation of this product depends on the greater reactivity of 1° substrates in S_N2 reactions.)

(c) 

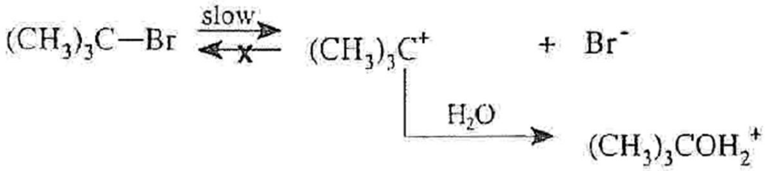
(Here two S_N2 reactions produce a cyclic molecule.)

(d) 
Cl-CH$_2$CH$_2$CH$_2$CH$_2$OH
+ NaH
-H$_2$
Et$_2$O
Cl-CH$_2$CH$_2$CH$_2$CH$_2$O$^-$
O

(e) 

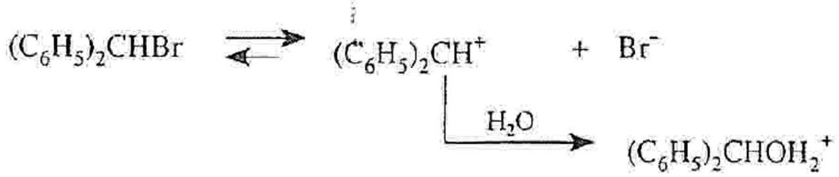
6.34 *ter*-Bütil bromür S_N1 hidrolizine uğradığında, sulu çözeltiye ortak iyon içeren bir bileşik, örneğin NaBr ilave etmenin tepkime hızı üzerine bir etkisi yoktur. Diğer yandan, $(C_6H_5)_2CHBr$ S_N1 hidrolizine uğratıldığında, NaBr ilavesi tepkimeyi yavaşlatır. $(C_6H_5)_2CH^+$ katyonunun $(CH_3)_3C^+$ katyonundan çok daha kararlı olduğu bilinir (niçin böyle olduğunu Altbölüm 15.12A'da göreceğiz); bu durumda, bu iki bileşiğin farklı davranışını açıklayınız.

6.34 The rate-determining step in the S_N1 reaction of *tert*-butyl bromide is the following:



$(CH_3)_3C^+$ is so unstable that it reacts almost immediately with one of the surrounding water molecules, and, for all practical purposes, no reverse reaction with Br^- takes place. Adding a common ion (Br^- from NaBr), therefore, has no effect on the rate.

Because the $(C_6H_5)_2CH^+$ cation is more stable, a reversible first step occurs and adding a common ion (Br^-) slows the overall reaction by increasing the rate at which $(C_6H_5)_2CH^+$ is converted back to $(C_6H_5)_2CHBr$.



6.35 Aşağıdaki alkil halojenürler, etanol ve su karışımı içerisinde (%80 C_2H_5OH/%20 H_2O) 55 °C'da hidrolize tabi tutulduğunda, tepkime hızları aşağıdaki sırayı göstermektedir.

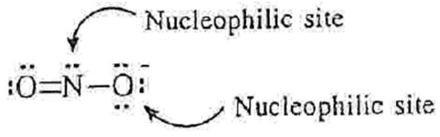
$$(CH_3)_3CBr > CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr$$

Etkinlik sırası için bir açıklama getiriniz.

6.35 Two different mechanisms are involved. $(CH_3)_3CBr$ reacts by an S_N1 mechanism, and apparently this reaction takes place faster. The other three alkyl halids react by an S_N2 mechanism, and their reactions are slower because the nucleophile (H_2O) is weak. The reaction rates of CH_3Br, CH_3CH_2Br, and $(CH_3)_2CHBr$ are affected by the steric hindrance, and thus their order of reactivity is $CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr$.

6.36 1° Alkil halojenürlerin nitrit tuzları ile tepkimesi RNO_2 ve RONO bileşiklerinin her ikisini de oluşturur. Bu davranışı açıklayınız.

6.36 The nitrite ion is an *ambident nucleophile;* that is, it is an ion with two nucleophilic sites. The equivalent oxygen atoms and the nitrogen atom are nucleophilic.

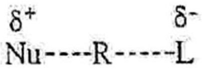


6.37 Çözücü polaritesinin artması, aşağıdaki nükleofilik yer değiştirme tepkimelerinin her birinin hızı üzerine nasıl bir etki yapar?

(a) $Nu: + R{-}L \longrightarrow R{-}Nu^+ + :L^-$

(b) $R{-}L^+ \longrightarrow R^+ + :L$

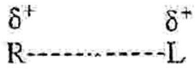
6.37 (a) The transition state has the form:



$$\overset{\delta^+}{Nu}\text{----}R\text{-----}\overset{\delta^-}{L}$$

in which charges are developing. The more polar the solvent, the better it can solvate the transition state, thus lowering the free energy of activation and increasing the reaction rate.

(b) The transition state has the form:

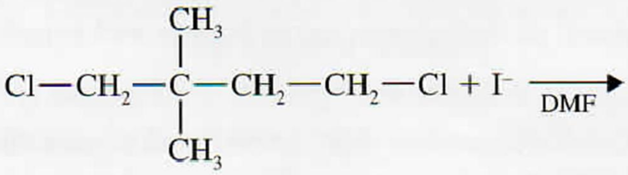


$$\overset{\delta^+}{R}\text{------------}\overset{\delta^+}{L}$$

in which the charge is becoming dispersed. A polar solvent is less able to solvate this transition state than it is to solvate the reactant. The free energy of activation, therefore, will become somewhat larger as the solvent polarity increases, and the rate will be slower.

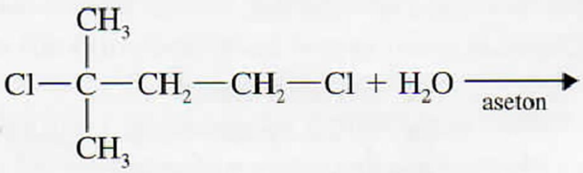
6.38 Aynı derişimdeki iki reaktantın aynı reaktif için veya bir reaktantın aynı moleküldeki iki reaktif için yarıştığı tepkimeler, yarışan tepkimelerdir. Aşağıdaki yarışan tepkimelerin her birinden oluşacak ana ürünü tahmin ediniz.

(a)



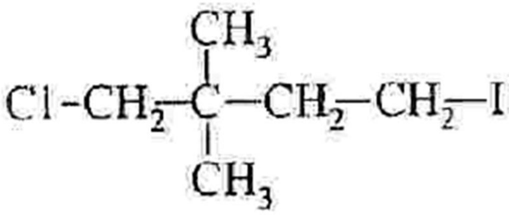
$$Cl{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH_2{-}CH_2{-}Cl + I^- \xrightarrow[DMF]{}$$

(b)



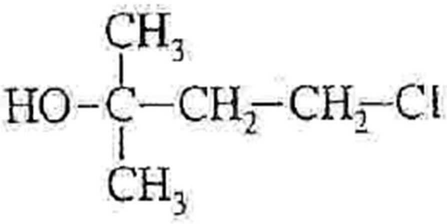
$$Cl{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH_2{-}CH_2{-}Cl + H_2O \xrightarrow[aseton]{}$$

6.38 (a)



$$Cl{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH_2{-}CH_2{-}I$$

(b)



$$HO{-}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}{-}CH_2{-}CH_2{-}Cl$$

+ some alkene

6.39 S_N2 Tepkimelerinin tersine, S_N1 tepkimeleri, nispeten daha az nükleofilik seçicilik gösterir. Yani, tepkime ortamında birden fazla nükleofil oldağunda, S_N1 tepkimeleri, zayıf nükleofillerle güçlü nükleofiller arasında çok az bir ayrım yapma eğilimi gösterir. Halbuki S_N2 tepkimeleri, belirgin bir ayrım yapma eğilimi gösterirler. **(a)** Bu davranışı açıklayınız. **(b)** $CH_3CH_2CH_2CH_2Cl$, 0,01 *M* NaCN ile etanol içerisindeki tepkimesi sonucu ana ürün olarak $CH_3CH_2CH_2CH_2CN$ oluştururken, aynı şartlarda $(CH_3)_3CCl$ nin ana ürün olarak $(CH_3)_3COCH_2CH_3$ oluşturmasını nasıl açıklarsınız?

6.39 (a) In an S_N1 reaction the carbocation intermediate reacts rapidly with any nucleophile it encounters in a Lewis acid–Lewis base reaction. In the case of the S_N2 reaction, the leaving group departs only when "pushed out" by the attacking nucleophile, and some nucleophiles are better than others.

(b) CN^- is a much better nucleophile than ethanol and hence the nitrile is formed in the S_N2 reaction of $CH_3CH_2CH_2CH_2Cl$. In the case of $(CH_3)_3CCl$ the *tert*-butyl cation reacts chiefly with the nucleophile present in higher concentration, here the ethanol solvent.

***6.40** Gaz fazında, *ter*-bütil klorürün karbon-klor bağının homolitik bağ ayrışma enerjisi (Altbölüm 10.2A), +328 kJ mol^{-1}; *ter*-bütil radikalinin iyonlaşma potansiyeli +715 kJ mol^{-1}; ve klorun elektron ilgisi -330 kJ mol^{-1}'dir. Bu verileri kullanarak, gaz fazında *ter*-bütil klorürün, *ter*-bütil katyon ve klorür iyonuna dönüşmesi için olan entalpi değişimini hesaplayınız (bulduğunuz değer, karbon-klor bağının heterolitik bağ ayrışma enerjisidir).

***6.40**

	ΔH°, kJ mol^{-1}	
$(CH_3)_3C{-}Cl \longrightarrow \cancel{(CH_3)_3C\cdot} + \cancel{Cl\cdot}$	+328	Homolytic bond dissoc. energy
$\cancel{(CH_3)_3C\cdot} \longrightarrow (CH_3)_3C^+ + \cancel{e^-}$	+715	Ionization potential
$\cancel{Cl\cdot} + \cancel{e^-} \longrightarrow Cl^-$	−330	Electron affinity
$(CH_3)_3C{-}Cl \longrightarrow (CH_3)_3C^+ + Cl^-$	+713	Heterolytic bond dissoc. energy

***6.41** *Gaz fazında*, kloroetanın, etanol ve hidrojen klorür oluşturmak üzere su ile tepkimesinde, $\Delta H^\circ = +26{,}6$ kJ mol^{-1} ve $\Delta S^\circ = +4.81$ J K^{-1} mol^{-1}'dir (25 °C'da). **(a)** İki terimden hangisi tepkimenin gerçekleşmesi için lehtedir? **(b)** Tepkime için ΔG°'yi hesaplayınız. Şimdi tepkimenin gerçekleşip gerçekleşmeyeceği hususunda ne söyleyebilirsiniz? **(c)** Tepkime denge sabitini hesaplayınız. **(d)** Sulu çözeltideki tepkime denge sabiti, şimdi hesapladığınızdan çok daha büyüktür. Bunu nasıl açıklarsınız?

***6.41** (a) The entropy term is slightly favorable. (The enthalpy term is highly unfavorable.)

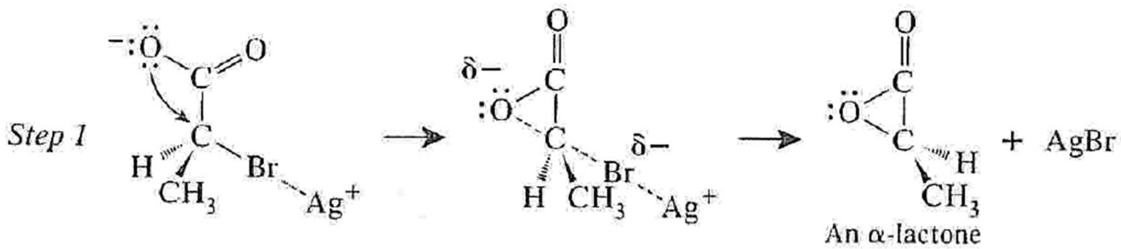
(b)
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 26.6\ \text{kJ mol}^{-1} - (298)(0.00481\ \text{kJ mol}^{-1}) \\ &= 25.2\ \text{kJ mol}^{-1}\end{aligned}$$

(c)
$$\begin{aligned}\log K_{eq} &= \frac{-\Delta G^\circ}{2.303RT} \\ &= \frac{-25.2\ \text{kJ mol}^{-1}}{(2.303)(0.008314\ \text{kJ mol}^{-1}\ \text{K}^{-1})(298\ \text{K})} \\ &= -4.4165 \\ K_{eq} &= 10^{-4.4165} = 3.85 \times 10^{-5}\end{aligned}$$

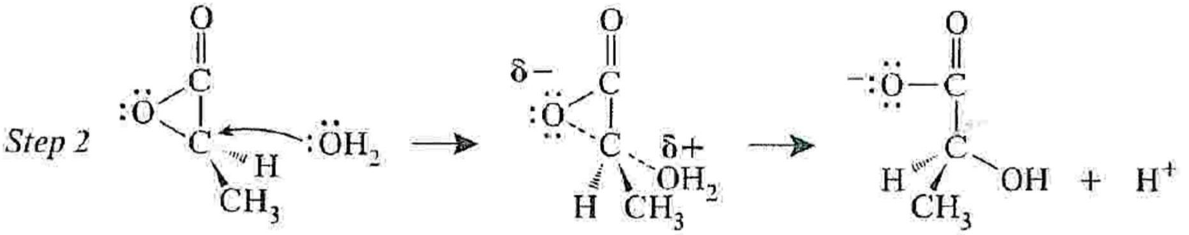
(d) The equilibrium is very much more favorable in aqueous solution because solvation of the products (ethanol, hydronium ions, and chloride ions) takes place and thereby stabilizes them.

***6.42** (*S*)-2-Bromopropanoik asit [(*S*)-$CH_3CHBrCO_2H$)] derişik sodyum hidroksit ile tepkime verdiğinde, (asitlendirmeden sonraki) ürün, yaygın olarak (*R*)-laktik asit olarak bilinen (*R*)-2-hidroksipropanoik asittir [(*R*)-$CH_3CHOHCO_2H$)] Elbette bu S_N2 tepkimesinden beklenen stereokimyasal olarak normal bir sonuçtur. Fakat, aynı tepkime, Ag_2O beraberliğinde (burada Ag^+, bir Lewis asidi rolü görür) seyreltik hidroksit iyonu ile gerçekleştirildiğinde *konfigürasyon aynı kalır* ve (*S*)-2-hidroksipropanoik asit oluşur. Bu tepkimenin mekanizması, *komşu grup katılımı* olarak adlandırılan bir olay içerir. Ag^+ ve seyreltik sodyum hidroksit kullanıldığında, net olarak konfigürasyon korunur. Bu tepkime için ayrıntılı bir mekanizma yazınız.

***6.42** The mechanism for the reaction involves the participation of the carboxylate group. In step 1 (see following reaction) an oxygen of the carboxylate group attacks the stereocenter from the backside and displaces bromide ion. (Silver ion aids in this process in much the same way that protonation assists the ionization of an alcohol.) The configuration of the stereocenter inverts in step 1, and a cyclic ester called an α-lactone forms.

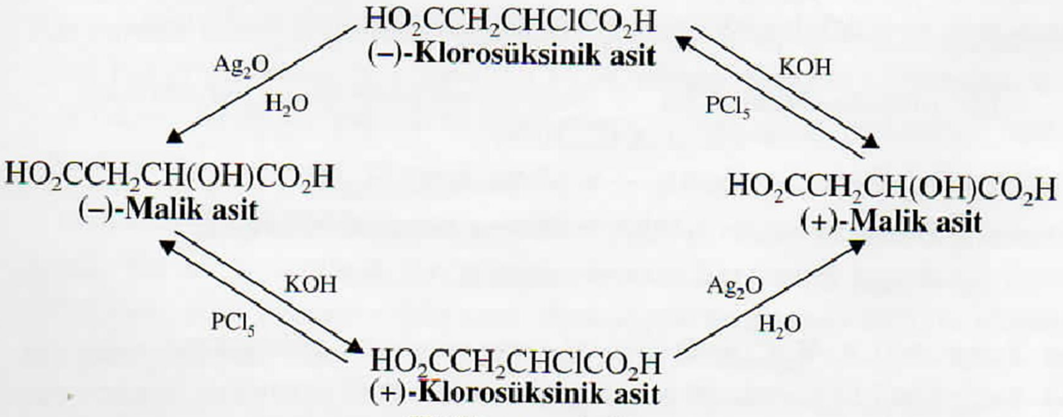


The highly strained three-membered ring of the α-lactone opens when it is attacked by a water molecule in step 2. *This step also takes place with an inversion of configuration.*



The net result of two inversions (in steps 1 and 2) is an overall *retention of configuration.*

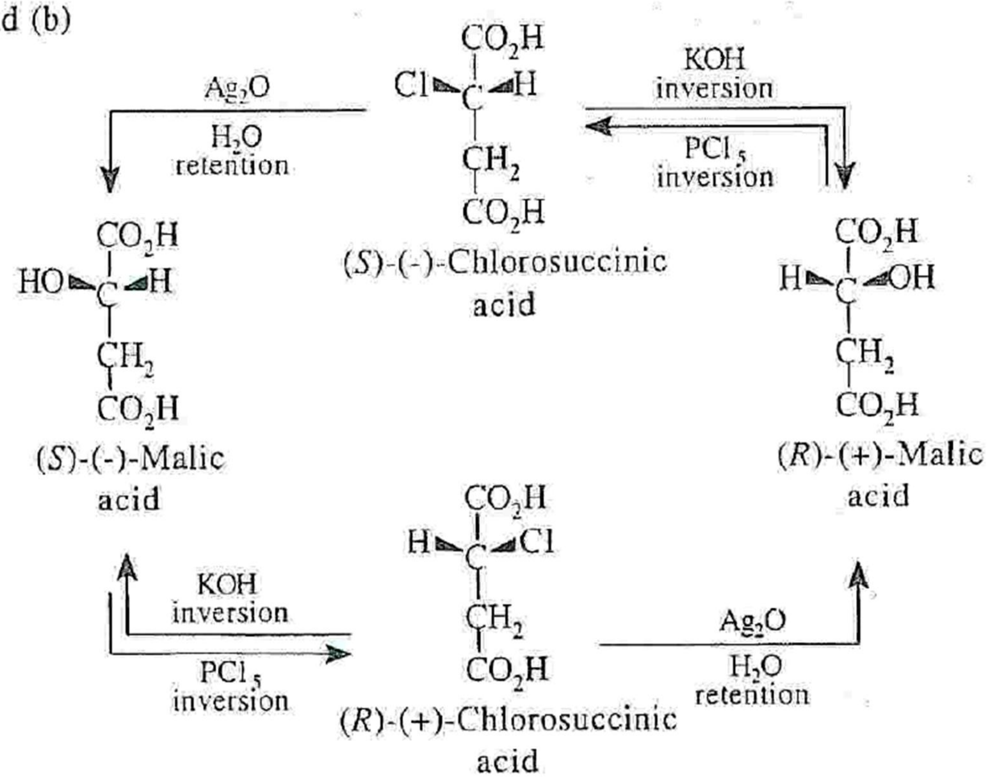
***6.43** Bir kimyasal tepkimedeki konfigürasyon devrilmesi olgusu, 1896'da Paul von Walden tarafından bulundu (Altbölüm 6.7). Walden'in konfigürasyon devrilmesi kanıtları aşağıdaki çevrime dayanmaktaydı:



Walden çevrimi

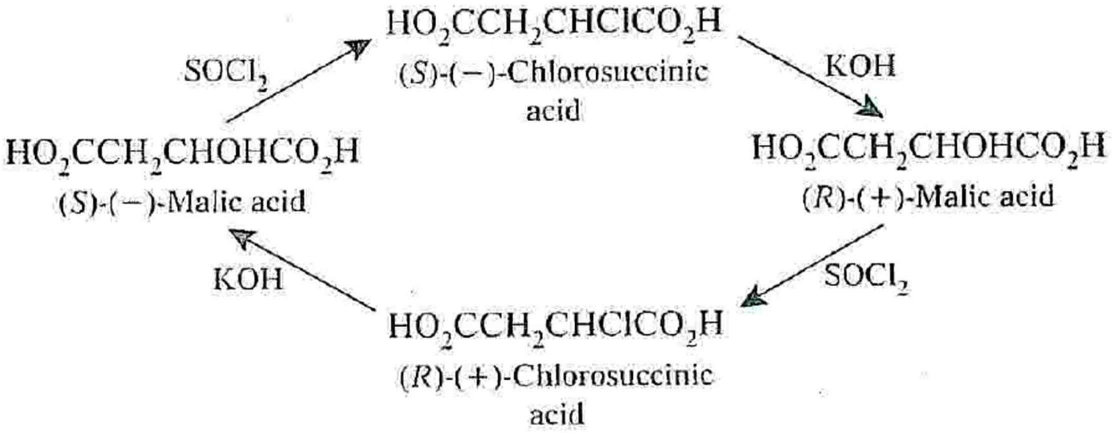
(a) Bir önceki problemdeki cevabınıza dayalı olarak, Walden çevrimindeki hangi tepkime muhtemelen konfigürasyon devrilmesi ile, hangi tepkime muhtemelen konfigürasyonun korunması ile olmaktadır? **(b)** Eksi optik çevirmeye sahip malik asitin (*S*) konfigürasyona sahip olduğu şimdi biliniyor. Walden çevrimindeki diğer bileşiklerin konfigurasyonları nedir? **(c)** Walden, (+)malik asidin PCI_5 yerine tiyonil klorür ile muamele edilmesi ile tepkime ürününün (+)-klorosüksinik asit olduğunu da buldu. Bu sonucu nasıl açıklarsınız? **(d)** (−)-Malik asit ve tiyonil klorür tepkimesinin aynı stereokimyaya sahip olduğunu varsayarak, PCI_5 yerine tiyonil klorür kullanmak yoluyla Walden çevrimini yeniden yazınız.

*6.43 (a) and (b)



(c) The reaction takes place with retention of configuration.

(d)

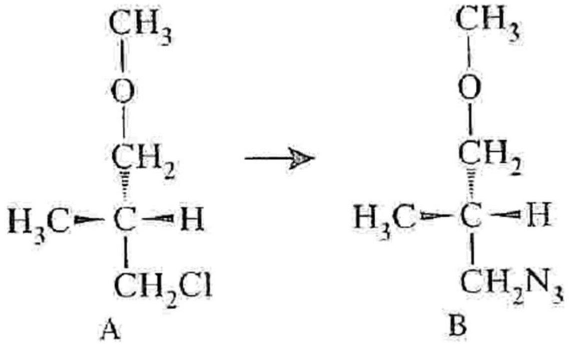


***6.44** (*R*)-(3-Kloro-2-metilpropil) metil eter (**A**), sulu etanol içerisindeki sodyum azür ile tepkimesi sonucu (*S*)-(3-azido-2-metilpropil) metil eter (**B**) verir. **A** Bileşiği, $ClCH_2CH(CH_3)CH_2OCH_3$ yapısına sahiptir.

(a) **A** ve **B**'nin her ikisi için de kama-çizgi formülünü gösteriniz.

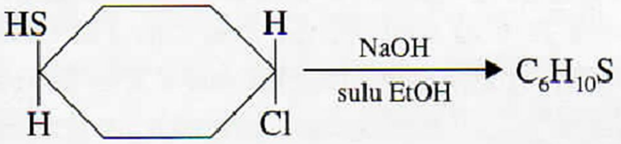
(b) Tepkime esnasında konfigürasyonda bir değişme olur mu?

***6.44**



No change of configuration occurs, just a change in the relative priority of a group at the stereocenter.

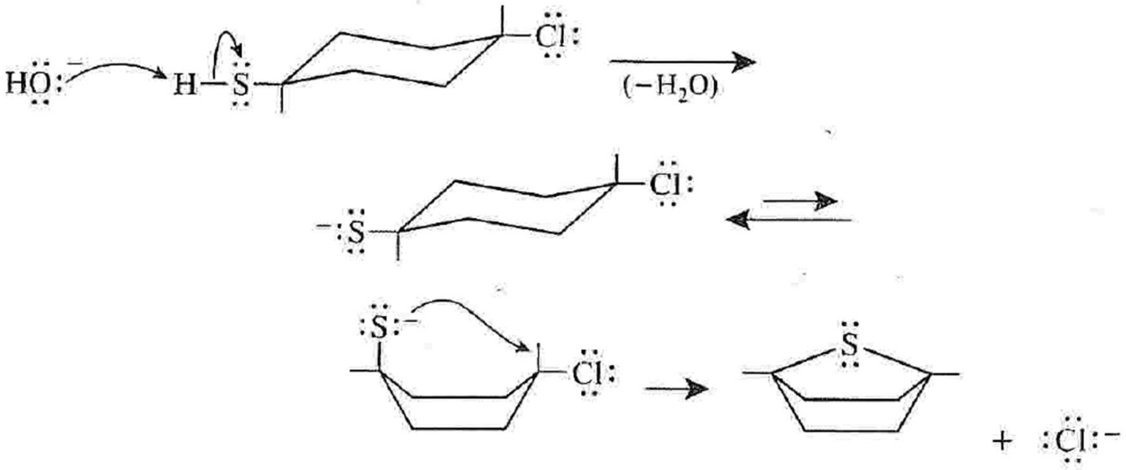
***6.45** Aşağıdaki tepkimeden çıkacak ürünün yapısını tahmin ediniz:



Ürün, 1620-1681 cm^{-1} bölgesinde kırmızı ötesi soğurma göstermemektedir.

***6.45** Comparison of the molecular formulas of starting material and product indicates a loss of HCl. The absence of IR bands in the 1620–1680 cm^{-1} region rules out the presence of the alkene function.

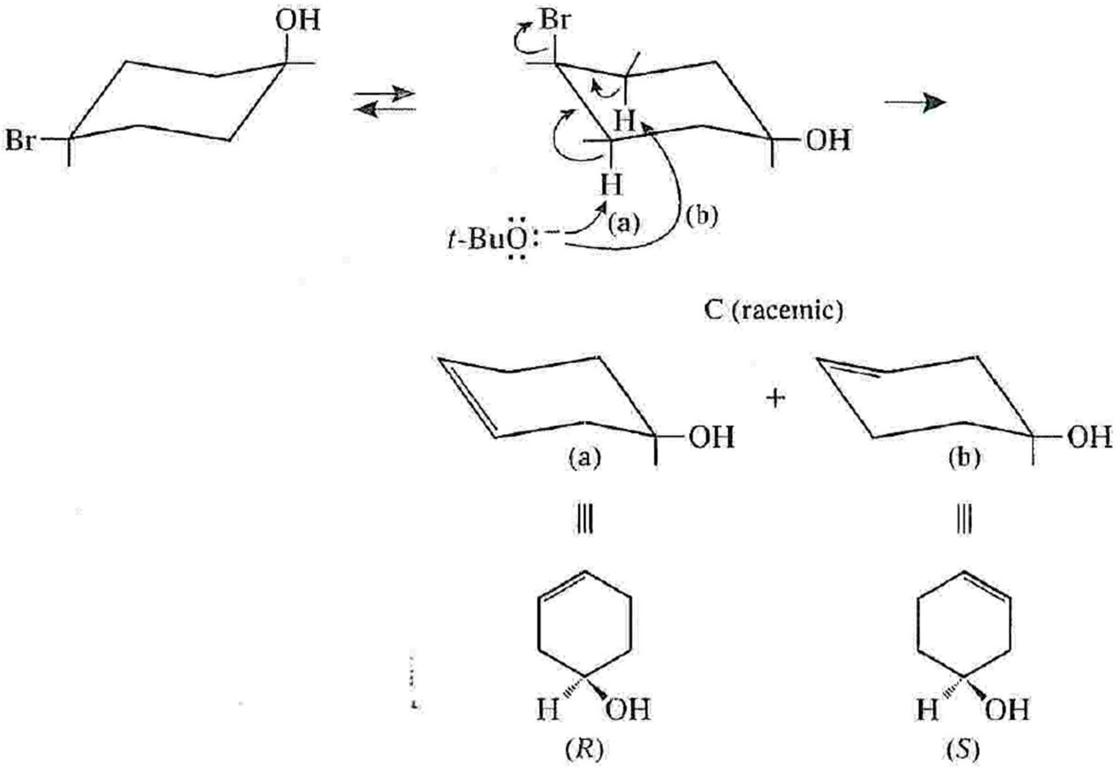
A nucleophilic substitution agrees with the evidence:



***6.46** *cis*-4-Bromosikloheksanol $\xrightarrow[\text{t-BuOH}]{\text{t-BuO}^-}$ rasemik $C_6H_{10}O$ (**C** bileşiği)

C Bileşiği, 1620-1680 cm^{-1} bölgesinde kırmızı ötesi soğurmaya sahiptir. **C** ürününü yazınız ve (*R*) ve (*S*) enantiyomerlerini tanımlayınız.

***6.46** The IR evidence indicates that C possesses both an alkene function and a hydroxyl group. An E2 reaction on this substrate produces enantiomeric unsaturated alcohols.

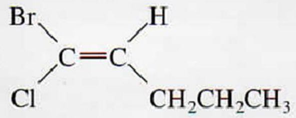


Alkenler ve Alkinler I: Özellikleri ve Elde Edilişleri. Alkil Halojenürlerin Ayrılma Tepkimeleri

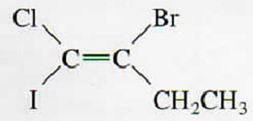
Problem 7.1

(*E*)–(*Z*) Adlandırma sistemini kullanarak [ayrıca, (e) ve (f) şıklarında (*R*–*S*) adlandırma sistemini de gözönüne alarak) aşağıdaki her bir bileşiğin IUPAC adını yazınız.

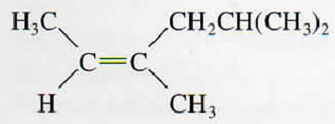
(a)



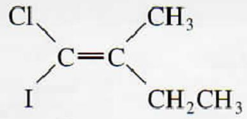
(b)



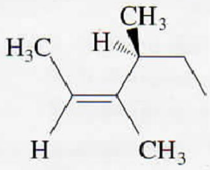
(c)



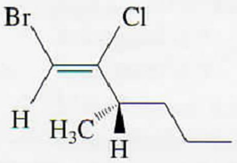
(d)



(e)



(f)



10.28 1894 yılında İngiliz Kimyacı H. J. H Fenton'un açıkladığı gibi, hidrojen peroksitle ferröz sülfat) tepkimeye girerek hidroksil (HO·) radikalini oluştururlar. Bu şekilde elde edelin HO· ile *ter*-bütil alkol etkileştirilirse, erime noktası 92°C olan kristal yapıda bir **X** maddesi elde edilmektedir. Spektral özellikleri aşağıda verilen **X** bileşiğinin yapısını bulunuz ve oluşum tepkimesinin mekanizmasını yazınız.

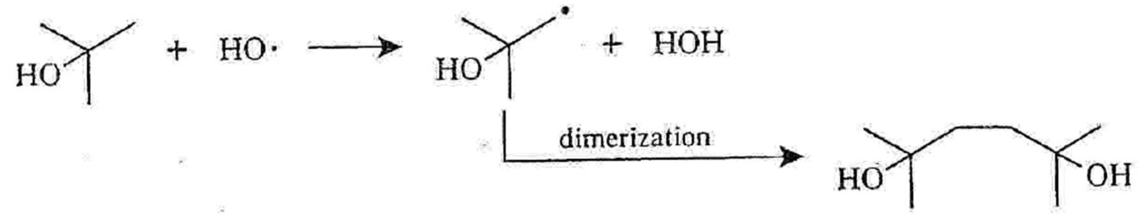
MS: kütle değeri en büyük olan pik 131 m/z de ortaya çıkıyor.

IR: 3620, 3550 (geniş), 2980, 2940, 1385, 1370 cm^{-1}

^1H NMR: δ 1,22, 1,58 ve 2,95'te keskin birliler (alan oranları 6 : 2 : 1)

^{13}C NMR: δ 28 (CH_3), 35 (CH_2), 68 (C)

*10.28



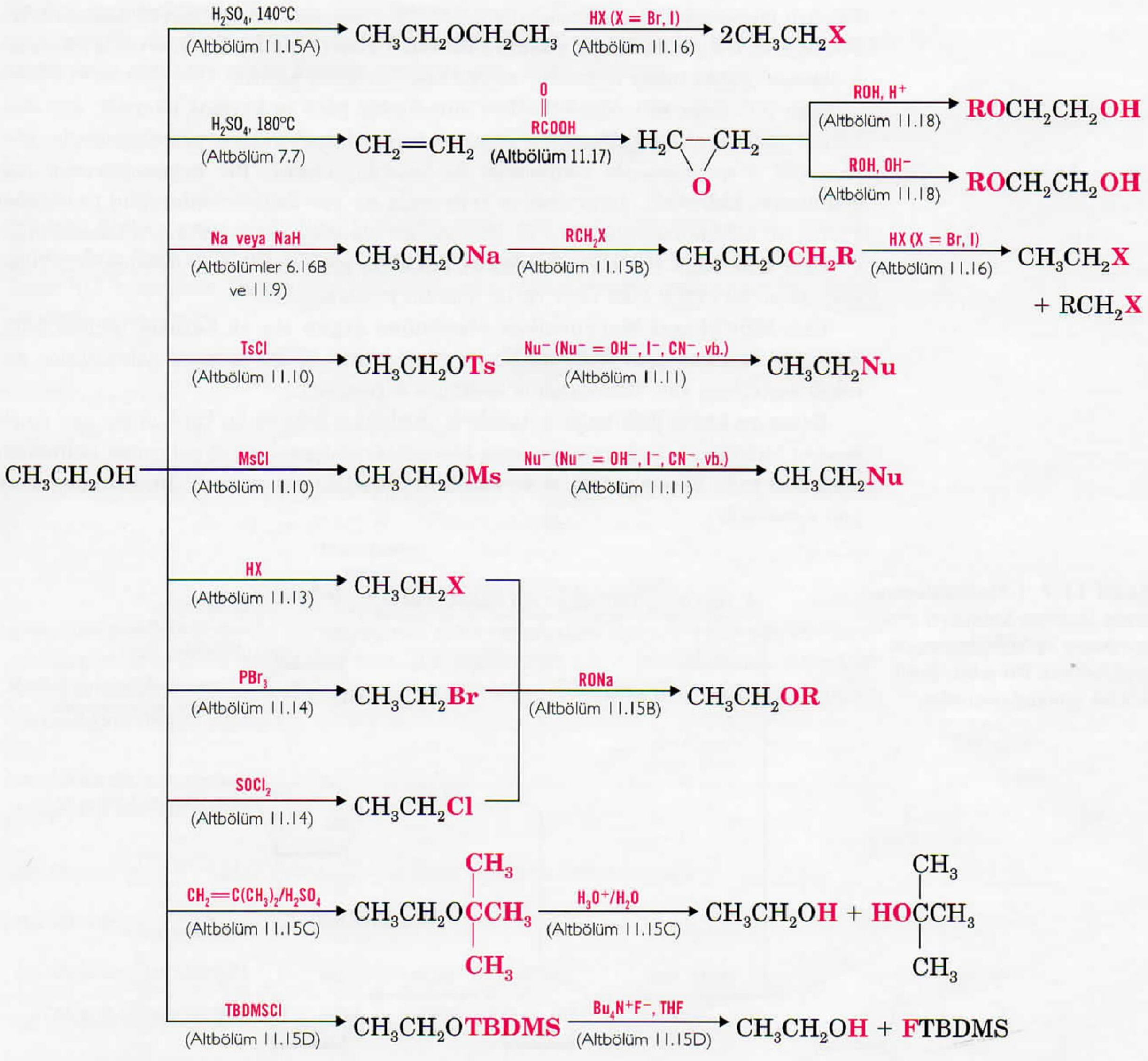
X

Alkoller ve Eterler

11.21 ALKENLERİN, ALKOLLERİN VE ETERLERİN TEPKİMELERİNİN ÖZETİ

Bu bölümde ve 8. Bölümde, sentez tasarımında son derece yararlı olabilecek tepkimeleri inceledik. Alkolleri ve eterleri kapsayan bu tepkimelerin çoğu Çizelge 11.6 da özetlenmiştir. Alkil halojenürleri, sülfonat esterleri, eterleri ve alkenleri elde etmek için alkolleri kullanabiliriz. Epoksitleri, diolleri, aldehitleri, ketonları ve karboksilik asitleri (özel alkenlere ve koşullara bağlı olarak) elde etmek için alkenleri yükseltgeyebiliriz. Alkanları, alkolleri ve alkil halojenürleri elde etmek için de alkenleri kullanabiliriz. Eğer elimizde, uygun bir komşu dihalojenürden elde edilebilecek bir uç alkin varsa, bundan türetilen alkinür iyonunu, nükleofilik yer değiştirme

Bazı sentez aletleri



Şekil 11.6 Alkollerin ve eterlerin etanolle başlayan önemli tepkimelerinin özeti.

ile karbon-karbon bağı oluşturmada kullanabiliriz. Şimdi elimizde şu ana kadar incelediğimiz tüm fonksiyonel grupları doğrudan ya da dolaylı birbirlerine dönüştürecek bir tepkime repertuarı bulunmaktadır. Altbölüm 11.21A'da alkenlerin bazı tepkimeleri özetlenecektir.

11.21A Sentezlerde Alkenler

Gerçekte alkenler, incelemiş olduğumuz diğer fonksiyonel grupların hepsinin elde edilmesinde giriş (anahtar) noktasıdır. Bu nedenle, tepkimelerin büyük çoğunluğu bize, ürünün konum kimyasal ve/veya stereokimyasal şeklinin kontrolü imkanını sağladığından, alkenler, sentezlerde çok yönlü ara ürünlerdir. Örneğin, eğer biz **bir ikili bağa Markovnikov yönelimi uyarınca su katmak** istersek, bunu gerçekleştirmek için üç yöntemden yararlanırız: (1) *oksiciva katılması-civa ayrılması* (Altbölüm 11.5), (2) *asit katalizli hidrasyon* (Altbölüm 8.5) ve (3) *sülfürik asit katılmasını izleyen hidroliz* (Altbölüm 8.4). Bu yöntemlerden oksiciva katılması-civa ayrılması laboratuvarda en yararlı olanıdır; çünkü kolay uygulanır ve *çevrilme meydana gelmez.*

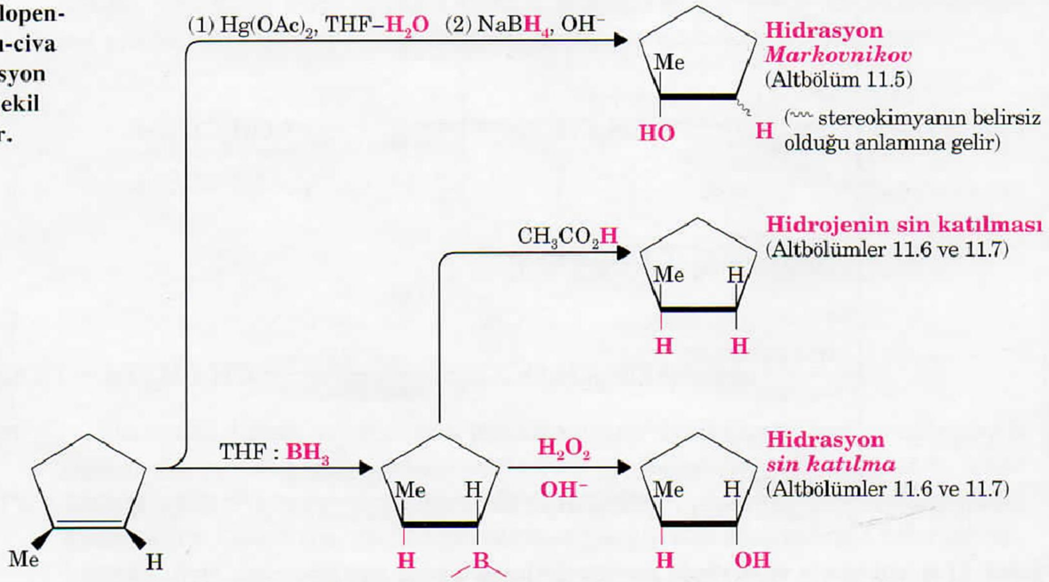
Eğer ikili bağa **anti–Markovnikov yönelimine göre su katmak istersek**, *hidroborasyon-yükseltgemeyi* kullanırız (Altbölüm 11.7). Hidroborasyon-yükseltgemeyle, *H— ve —OH gruplarının sin katılmasını* da başarmış oluruz. **Bir organoboranın bor grubunun, hidroksil, döteryum ve trityumla da yer değiştirebileceğini** (Altbölüm 11.7B) ve hidroborasyonun *H— ve -B—'nin bir sin katılmasını* içerdiğini hatırlayınız.

Eğer **ikili bağa HX'i Markovnikov kuralına göre katmak** (Altbölüm 8.2) istersek, alkeni HF, HCl, HBr veya HI ile tepkimeye sokarız.

Eğer **HBr'yi anti Markovnikov yönelimine uygun olarak katmak** istersek (Altbölüm 10.9), alkeni HBr *ve bir peroksitle* etkileştiririz. (Diğer hidrojen halojenürler, peroksit varlığında anti Markovnikov katılması vermezler).

Brom ve kloru ikili bağa katabiliriz (Altbölüm 8.6) ve bu katılma bir *anti katılmadır* (Altbölüm 8.7). Bromlama veya klorlamayı su içerisinde uygulayarak (Altbölüm 8.8), ikili bağa **X—ve —OH'yi de katabiliriz** (halohidrin sentezi). Bu katılma da *bir anti katılmadır*.

tilsiklopen-
ılması-civa
borasyon
kil, Şekil
cısıdır.


(1) Hg(OAc)$_2$, THF–H$_2$O (2) NaBH$_4$, OH$^-$
Me
HO
H
Hidrasyon
Markovnikov
(Altbölüm 11.5)
(〰 stereokimyanın belirsiz olduğu anlamına gelir)
CH$_3$CO$_2$H
Me
H
H
H
Hidrojenin sin katılması
(Altbölümler 11.6 ve 11.7)
THF : BH$_3$
Me
H
H
B
H$_2$O$_2$
OH$^-$
Me
H
H
OH
Hidrasyon
sin katılma
(Altbölümler 11.6 ve 11.7)
Me
H

Eğer **ikili bağın sin hidroksillemesini** gerçekleştirmek istersek, ya $KMnO_4$'ün soğuk bazik çözeltisini veya OsO_4 ile tepkimeyi izleyen $NaHSO_3$ muamelesini kullanırız (Altbölüm 8.10). Bu iki yöntemden sonuncusu tercih edilebilir; çünkü $KMnO_4$, alkeni aşırı yükseltgeyerek ikili bağın bölünmesine de yol açabilir.

Bir ikili bağın anti hidroksillenmesi, alkeni önce bir "*epokside*" dönüştürmek ve ardından asit katalizli hidroliz uygulamakla gerçekleştirilir (Altbölüm 11.19).

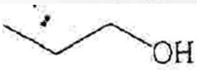
Bu tepkimelerin çoğunun eşitlikleri Şekil 8.3 ve 11.7'de verilmiştir.

"İzopropanol" ve "*ter*-bütanol" gibi adların kullanılmasındaki yanlışlık nedir? ◄ **Problem 11.1**

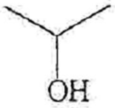
11.1 These names mix two systems of nomenclature (radicofunctional and substitutive; see Section 4.3F). The proper names are: isopropyl alcohol (radicofunctional) or 2-propanol (substitutive), and *tert*-butyl alcohol (radicofunctional) and 2-methyl-2-propanol (substitutive). Names with mixed systems of nomenclature should not be used.

Problem 11.2 ➤ Molekül formülleri (a) C_3H_8O ve (b) $C_4H_{10}O$ olan tüm alkollerin ve eterlerin bağ-çizgi formüllerini yazınız ve adlandırınız.

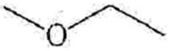
11.2 (a)



1-Propanol
(Propyl alcohol)

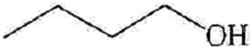


2-Propanol
(Isopropyl alcohol)

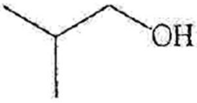


Methoxyethane
(Ethyl methyl ether)

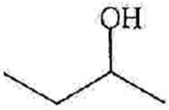
(b)



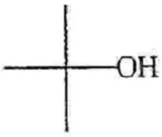
1-Butanol
(Butyl alcohol)



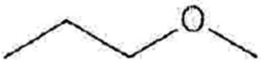
2-Methyl-1-propanol
(Isobutyl alcohol)



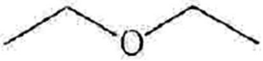
2-Butanol
(*sec*-Butyl alcohol)



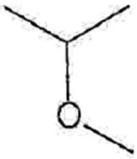
2-Methyl-2-propanol
(*tert*-Butyl alcohol)



1-Methoxypropane
(Methyl propyl ether)



Ethoxyethane
(Diethyl ether)



2-Methoxypropane
(Isopropyl methyl ether)

Problem 11.3 ➤ 1,2-Propandiol ve 1,3-propandiolün (sırasıyla propilen glikol ve trimetilen glikol, bkz. Çizelge 11.2) kaynama noktaları bütil alkollerin ve hatta molekül kütleleri yaklaşık aynı olan tüm diğer bileşiklerin kaynama noktalarından daha yüksektir. Bu durumu nasıl açıklarsınız?

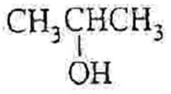
11.3 The presence of two $-OH$ groups in each molecule of 1,2-propanediol and 1,3-propanediol allows their molecules to form more hydrogen bonds. Greater hydrogen-bond formation means that the molecules of 1,2-propanediol and 1,3-propanediol are more highly associated, and, consequently, their boiling points are higher.

Problem 11.4 ➤ Aşağıdaki alkenleren asit-katalizli su katılmasından hangi ürünler oluşur?

(a) Eten
(b) Propen
(c) 2-Metilpropen
(d) 2-Metil-1-büten

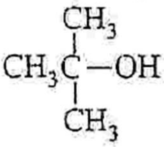
$\boxed{11.4}$ (a) CH_3CH_2OH

(b)



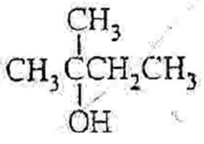
$CH_3\underset{OH}{C}HCH_3$

(c)



$CH_3\overset{CH_3}{\underset{CH_3}{C}}-OH$

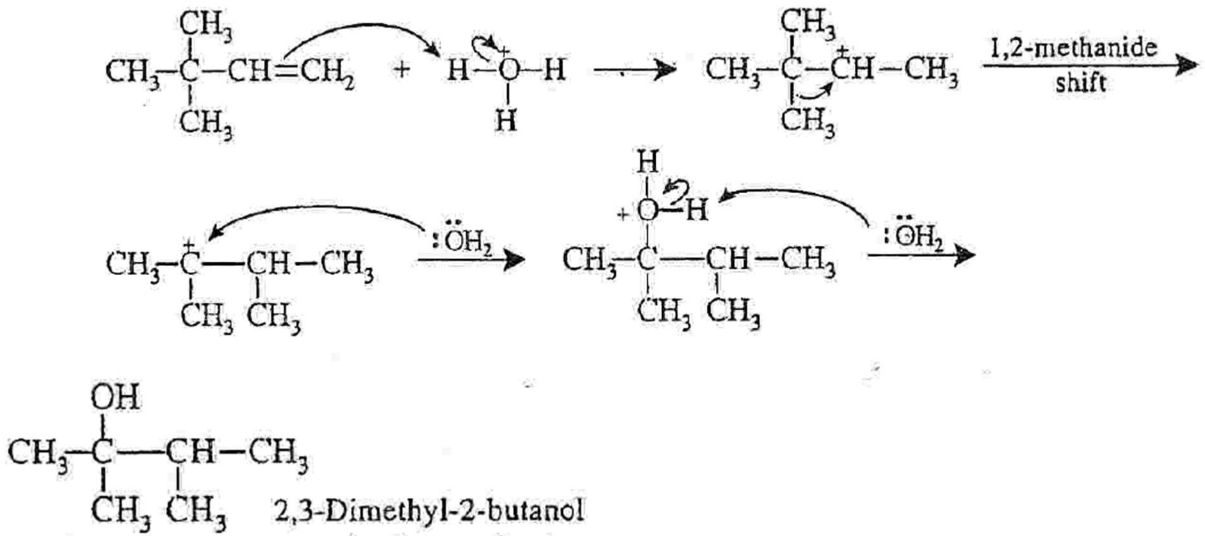
(d)



$CH_3\overset{CH_3}{\underset{OH}{C}}CH_2CH_3$

Problem 11.5 ➤ 3,3-Dimetil-1-bütenin sulu sülfürik asitle tepkimeye sokulması, 3,3-dimetil-2-bütanol eldesi için başarılı bir yöntem değildir; çünkü izomerik bileşik ana ürün olarak oluşur. Bu izomerik bileşik nedir ve nasıl oluşur?

11.5 A rearrangement takes place.

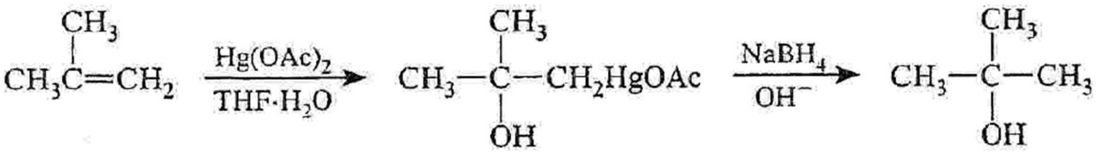


2,3-Dimethyl-2-butanol
(major product)

Uygun bir alkenden başlayarak, aşağıdaki alkollerin oksiciva katılması–civa ayrılması tepkimesiyle sentezinin tüm basamaklarını gösteriniz. ➤ **Problem 11.6**

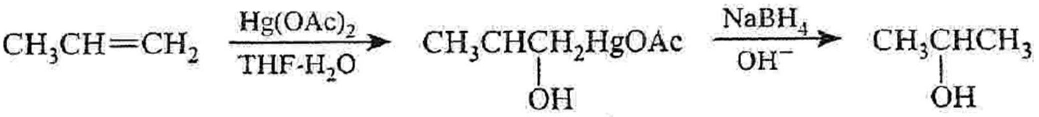
(a) *ter*-Bütilalkol (b) İzopropil alkol (c) 2-Metil-2-bütanol

11.6 (a)



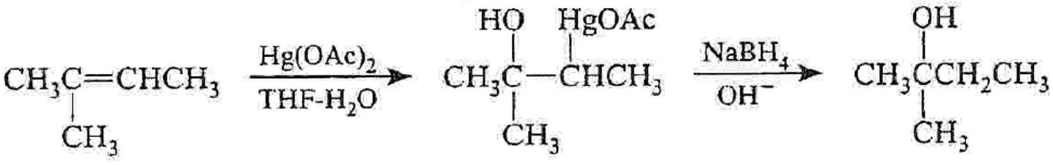
$CH_3\overset{CH_3}{C}=CH_2 \xrightarrow[THF\text{-}H_2O]{Hg(OAc)_2} CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2HgOAc \xrightarrow[OH^-]{NaBH_4} CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3$

(b)



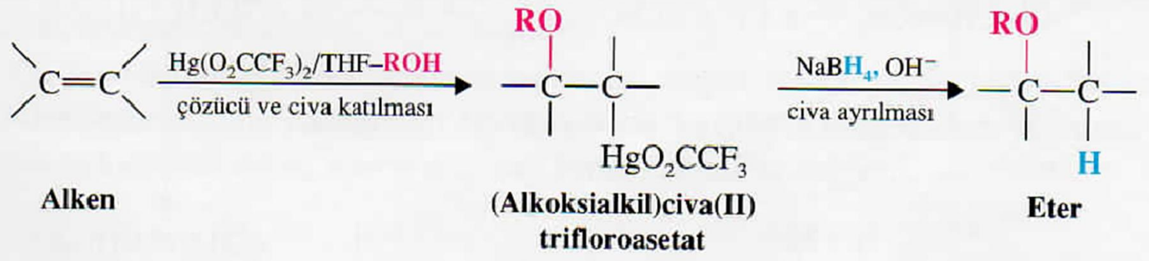
$CH_3CH=CH_2 \xrightarrow[THF\text{-}H_2O]{Hg(OAc)_2} CH_3\underset{OH}{C}HCH_2HgOAc \xrightarrow[OH^-]{NaBH_4} CH_3\underset{OH}{C}HCH_3$

(c)



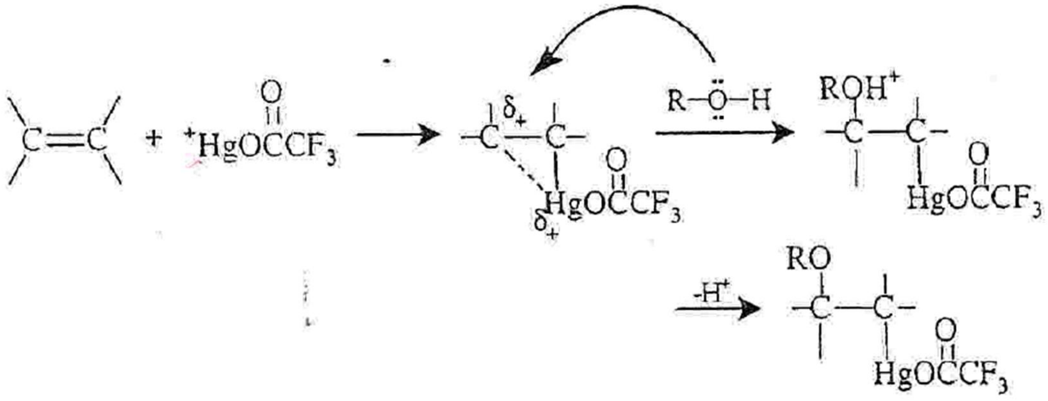
$CH_3\underset{CH_3}{C}=CHCH_3 \xrightarrow[THF\text{-}H_2O]{Hg(OAc)_2} CH_3\overset{HO}{\underset{CH_3}{C}}-\overset{HgOAc}{C}HCH_3 \xrightarrow[OH^-]{NaBH_4} CH_3\overset{OH}{\underset{CH_3}{C}}CH_2CH_3$

Bir alken; bir alkol (ROH) içeren THF'de civa(II) trifloroasetatla tepkimeye sokulduğunda, bir (alkoksialkil)civa bileşiği meydana gelir. Bu ürün $NaBH_4/OH^-$ ile etkileştirildiğinde bir eter oluşur. Toplam süreç *çözücü ve civa katılması (solvomerkürasyon) - civa ayrılması (demerkürasyon)* olarak adlandırılır. ➤ **Problem 11.7**

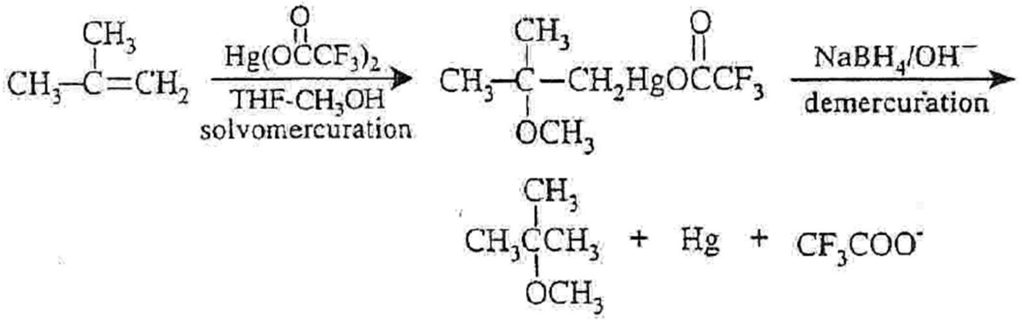


(a) Bu eter sentezinin çözücü ve civa katılması basamağının olası mekanizmasını açıklayınız. (b) Çözücü ve civa katılması - civa ayrılması işlemini, *ter*-bütil metil eter elde etmek için nasıl uygulayacağınızı gösteriniz.

11.7 (a)



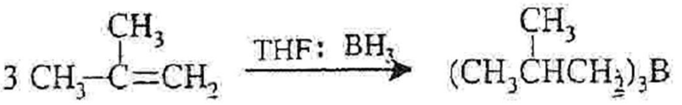
(b)



Problem 11.8 ➤ Uygun bir alkenden başlayarak, (a) tribütilboran (b) triizobütilboran ve (c) tri-*sek*-bütilboran sentezini açıklayınız; (d) 1-Metilsikloheksenin hidroborasyonunun stereokimyasını gösteriniz.

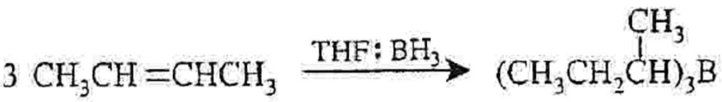
11.8 (a) $3\ CH_3CH_2CH{=}CH_2 \xrightarrow{THF:BH_3} (CH_3CH_2CH_2CH_2)_3B$

(b)



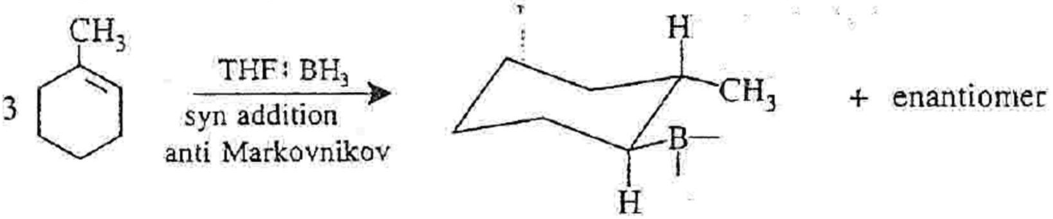
$3\ CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow{THF:\ BH_3} (CH_3\overset{CH_3}{C}HCH_2)_3B$

(c)



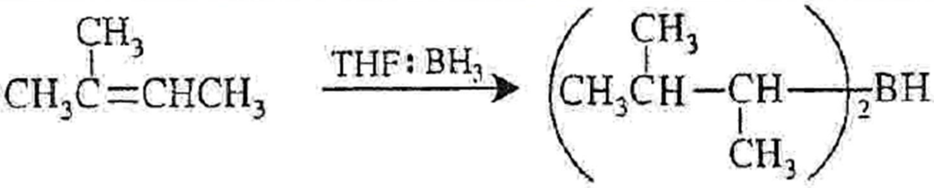
$3\ CH_3CH{=}CHCH_3 \xrightarrow{THF:BH_3} (CH_3CH_2\overset{CH_3}{C}H)_3B$

(d)



Problem 11.9 ➤ 2-Metil-2-büten gibi sterik engelli bir alken, THF:BH_3 ile etkileştirildiğinde, bir trialkilboran yerine bir dialkilboran meydana gelir. Eğer iki mol 2-metil-2-büten 1 mol BH_3'e katılırsa "disiamilboran" olarak da bilinen bir ürün oluşur. Yapısını gösteriniz. Disiamilboran, sterik engelli boranların gerekli olduğu sentezlerde yararlı bir reaktiftir. ("*Di*-*s*ekonder-*izo*-*amil*"den gelen "disiamil" adı hiç sistematik olmayan ve kabul görmeyen bir addır. "Amil" adı, beş karbonlu alkil grubunun eski yaygın adıdır.)

11.9



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow{THF:BH_3} \left(CH_3\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{CH_3}{|}}{CH}-\right)_2BH$$

Disiamylborane

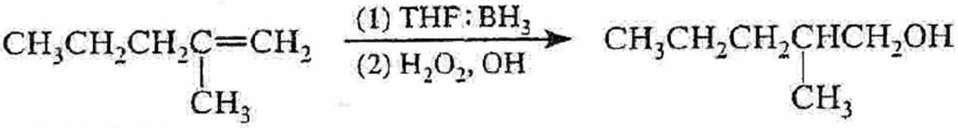
Problem 11.10 ➤ Uygun bir alkenle başlayarak aşağıdaki alkolleri, hidroborasyon–yükseltgeme tepkimesiyle nasıl elde edeceğinizi gösteriniz.

(a) 1-Pentanol
(b) 2-Metil-1-pentanol
(c) 3-Metil-2-pentanol
(d) 2-Metil-3-pentanol
(e) *trans*-2-Metilsiklobütanol

11.10 (a) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH_2CH_2CH_2CH_2OH$

1-Pentene

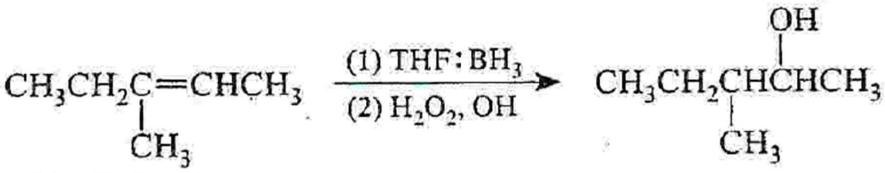
(b)



$$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2OH$$

2-Methyl-1-pentene

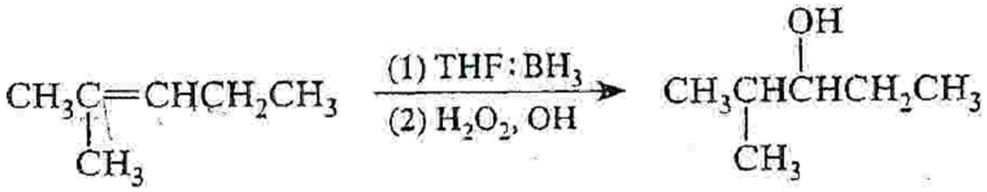
(c)



$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}{=}CHCH_3 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3CH_2\underset{\underset{CH_3}{|}}{C}H\overset{OH}{\overset{|}{C}H}CH_3$$

3-Methyl-2-pentene

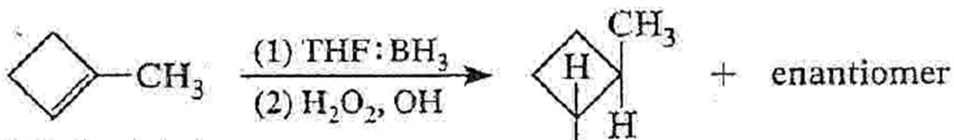
(d)



$$CH_3\underset{\underset{CH_3}{|}}{C}{=}CHCH_2CH_3 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF:BH_3} CH_3\underset{\underset{CH_3}{|}}{C}H\overset{OH}{\overset{|}{C}H}CH_2CH_3$$

2-Methyl-2-pentene

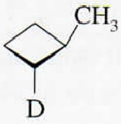
(e)



1-Methylcyclobutene

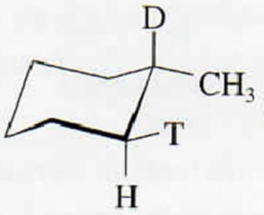
Gerekli herhangi bir alkenden (veya sikloalkenden) başlayarak ve elinizde döteryoasetik asit (CH_3CO_2D) bulunduğunu varsayarak, aşağıdaki döteryumla işaretlenmiş bileşiklerin sentezlerini tasarlayınız. ◀ **Problem 11.11**

(a) $(CH_3)_2CHCH_2CH_2D$ **(b)** $(CH_3)_2CHCHDCH_3$ **(c)**



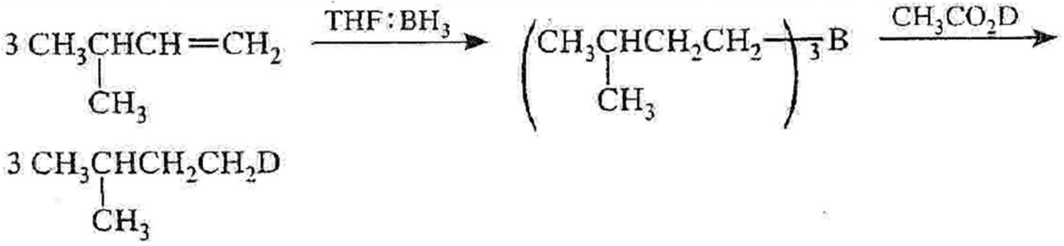
(+ enantiyomer)

(d) Yine elinizde THF:BD_3 ve CH_3CO_2T bulunduğunu varsayarak aşağıdaki bileşik için bir sentez öneriniz.



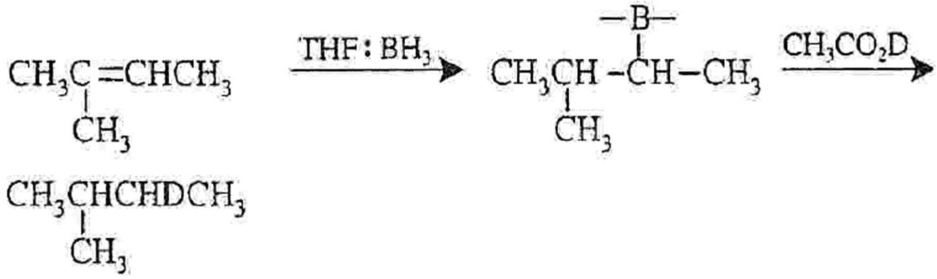
(+ enantiyomer)

11.11 (a)



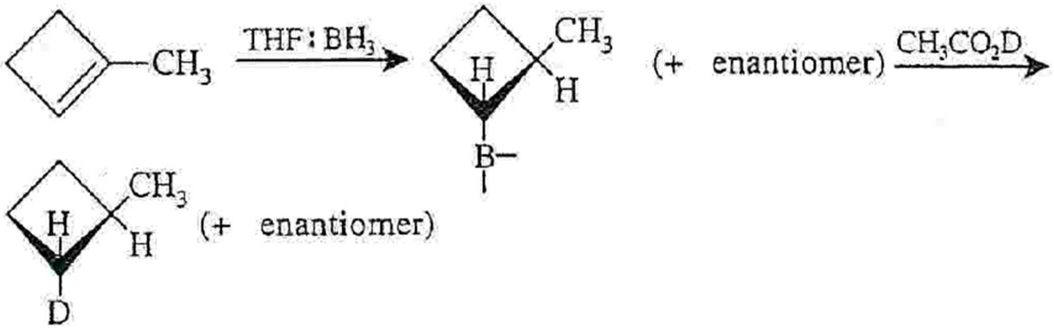
$$3\,\mathrm{CH_3\underset{CH_3}{C}HCH{=}CH_2} \xrightarrow{\mathrm{THF:BH_3}} \mathrm{(CH_3\underset{CH_3}{C}HCH_2CH_2\text{–})_3B} \xrightarrow{\mathrm{CH_3CO_2D}} 3\,\mathrm{CH_3\underset{CH_3}{C}HCH_2CH_2D}$$

(b)

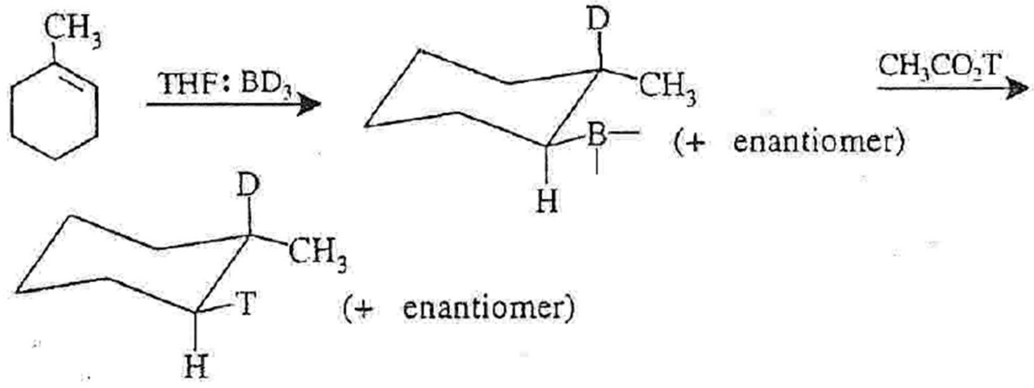


$$\mathrm{CH_3\underset{CH_3}{C}{=}CHCH_3} \xrightarrow{\mathrm{THF:BH_3}} \mathrm{CH_3\underset{CH_3}{C}H\text{–}\overset{\text{–B–}}{C}H\text{–}CH_3} \xrightarrow{\mathrm{CH_3CO_2D}} \mathrm{CH_3\underset{CH_3}{C}HCHDCH_3}$$

(c)



(d)



Problem 11.12

Aşağıda verilen bileşiklerin çözeltilerine etanol katıldığında meydana gelebilecek (eğer olursa) asit-baz tepkimelerinin eşitliklerini yazınız. Her tepkimedeki kuvvetli asit ve kuvvetli bazı işaretleyiniz. (a) Sodyum amit (b) Sodyum etinür ve (c) Sodyum asetat (Çizelge 3.1'i inceleyiniz).

11.12 (a)
$$\underset{\substack{\text{Stronger}\\ \text{acid}}}{CH_3CH_2OH} + \underset{\substack{\text{Stronger}\\ \text{base}}}{NaNH_2} \longrightarrow \underset{\substack{\text{Weaker}\\ \text{base}}}{CH_3CH_2ONa} + \underset{\substack{\text{Weaker}\\ \text{acid}}}{NH_3}$$

(b)
$$CH_3CH_2OH + HC{\equiv}CNa \longrightarrow CH_3CH_2ONa + HC{\equiv}CH$$

(c)
$$\underset{\substack{\text{Weaker}\\ \text{acid}}}{CH_3CH_2OH} + \underset{\substack{\text{Weaker}\\ \text{base}}}{NaOAc} \cancel{\longrightarrow} \underset{\substack{\text{Stronger}\\ \text{base}}}{CH_3CH_2ONa} + \underset{\substack{\text{Stronger}\\ \text{acid}}}{HOAc}$$

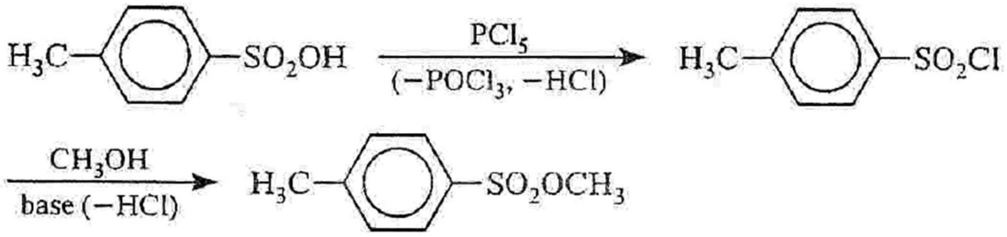
Problem 11.13 ➤ Bir izotopla işaretlenmiş bir alkol kullanarak, alkil sülfonat oluşumunda alkolün C—O bağının bölünmediğini gösteren bir deney öneriniz.

11.13 Use an alcohol containing labeled oxygen. If all of the label appears in the sulfonate ester, then one can conclude that the alcohol C–O bond does not break during the reaction:

$$R{-}^{18}O{-}H + R'{-}SO_2Cl \xrightarrow[\text{(-HCl)}]{\text{base}} R{-}^{18}O{-}SO_2{-}R'$$

Uygun sülfonik asit ve PCl_5 veya uygun sülfonil klorürlerle başlayarak (a) metil *p*-toluensülfonat (b) izobütil metansülfonat ve (c) *ter*-bütil metansülfonatı nasıl elde edebileceğinizi gösteriniz. ◄ **Problem 11.14**

11.14 (a)

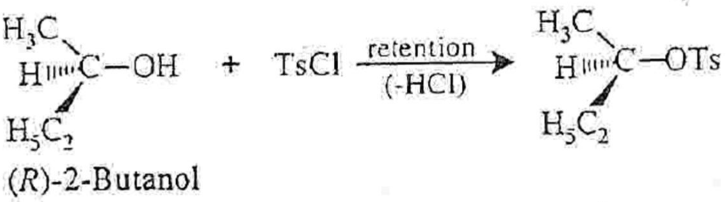


(b)
$$CH_3SO_2OH \xrightarrow[(-POCl_3,\ -HCl)]{PCl_5} CH_3SO_2Cl \xrightarrow[\text{base }(-HCl)]{(CH_3)_2CHCH_2OH} CH_3SO_2OCH_2CH(CH_3)_2$$

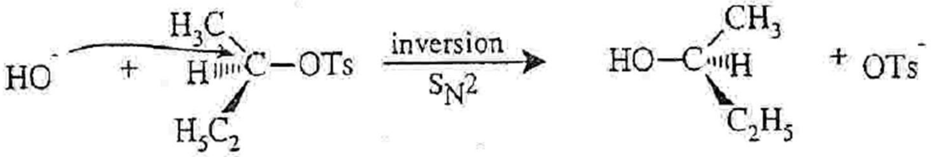
(c)
$$CH_3SO_2Cl \xrightarrow[\text{base (-HCl)}]{(CH_3)_3COH} CH_3SO_2OC(CH_3)_3$$

Problem 11.15 ➤ (a) (*R*)-2-Bütanol bir tosilata dönüştürüldüğünde ve (b) bu tosilat S_N2 yoluyla hidroksit iyonuyla tepkimeye girdiğinde, (c) *cis*-4-metilsikloheksanol tosilata dönüştürülüp, bu tosilat LiCl ile (uygun bir çözücüde) tepkimeye sokularak *trans*-1-kloro-4-metilsikloheksan oluşturulduğunda, oluşan ürünlerin konfigürasyonlarını belirtiniz. Bu basamakların stereokimyasını açıklayınız.

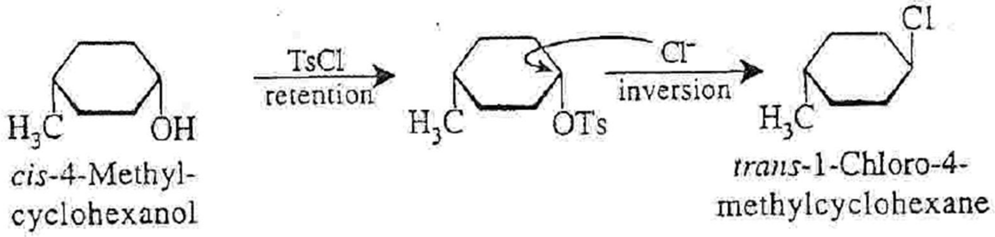
11.15 (a)



(b)

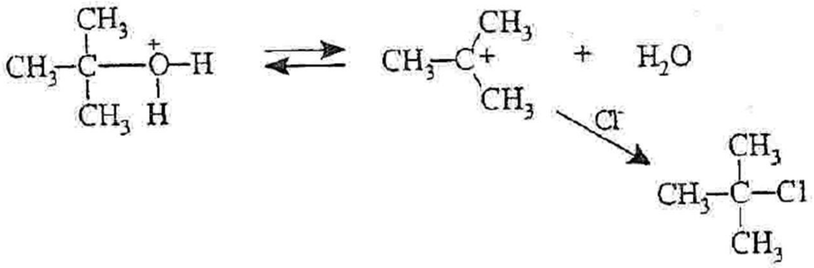


(c)



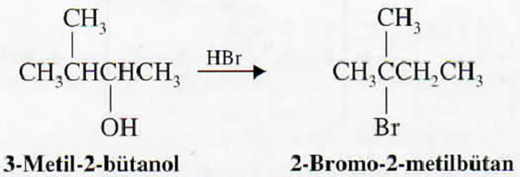
(a) Üçüncül alkollerin HX ile ikincil alkollerden daha hızlı tepkime vermesini nasıl açıklarsınız? (b) Metanolün HX ile bir birincil alkolden daha hızlı tepkime vermesini nasıl açıklarsınız? **Problem 11.16**

11.16 (a) Tertiary alcohols react faster than secondary alcohols because they form more stable carbocations; that is, 3° rather than 2°:

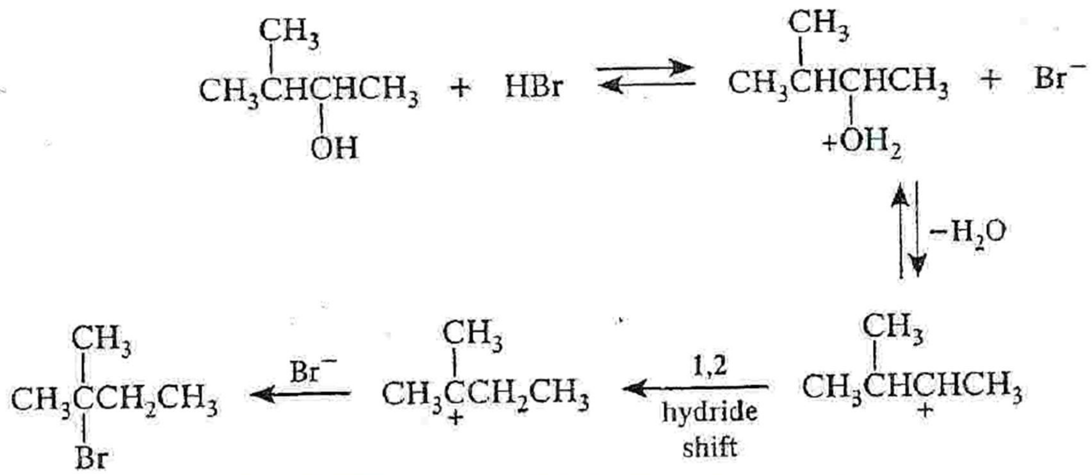


(b) CH_3OH reacts faster than 1° alcohols because it offers less hindrance to S_N2 attack. (Recall that CH_3OH and 1° alcohols must react through an S_N2 mechanism.)

3-Metil-2-bütanol (aşağı tepkimeye bakınız) HBr ile tek ürün olarak 2-bromo-2-metilbütanı verir. Tepkimenin mekanizmasını açıklayınız. **Problem 11.17**



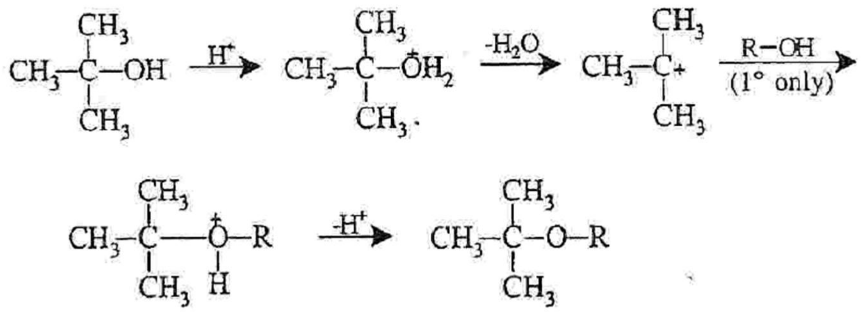
11.17



$$\mathrm{CH_3CH\overset{CH_3}{|}CHCH_3(\underset{|}{OH})} + \mathrm{HBr} \rightleftharpoons \mathrm{CH_3\overset{CH_3}{CH}\underset{+OH_2}{CH}CH_3} + \mathrm{Br^-} \xrightarrow{-\mathrm{H_2O}} \mathrm{CH_3\overset{CH_3}{CH}\underset{+}{CH}CH_3} \xrightarrow[\text{shift}]{\text{1,2 hydride}} \mathrm{CH_3\underset{+}{\overset{CH_3}{C}}CH_2CH_3} \xrightarrow{\mathrm{Br^-}} \mathrm{CH_3\underset{Br}{\overset{CH_3}{C}}CH_2CH_3}$$

Problem 11.13 ➤ Alkil gruplarından birinin *ter*-bütil, diğerinin bir birincil alkil grubu olduğu simetrik olmayan bir eter bileşiğinin sentezi, bu konuda yukarıda söylediklerimizin dışındadır. Bu sentez, oda sıcaklığında birincil alkol ve H_2SO_4 karışımına *ter*-bütil alkolün ilave edilmesiyle başarılabilir. Bu tepkime için olası bir mekanizma önerinizi ve bunun neden başarılı olduğunu açıklayınız.

11.18 (a)

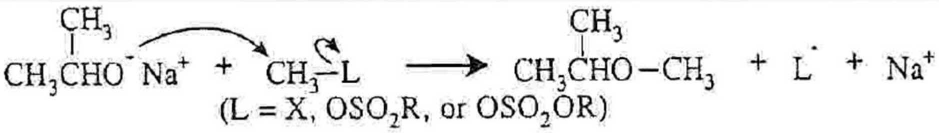


$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{+}{O}H_2} \xrightarrow{\mathrm{-H_2O}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{+}} \xrightarrow[(1^\circ\ \text{only})]{\mathrm{R{-}OH}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{H}{\overset{+}{O}}{-}R} \xrightarrow{\mathrm{-H^+}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}O{-}R}$$

This reaction succeeds because a 3° carbocation is much more stable than a 1° carbocation. Consequently, mixing the 1° alcohol and H_2SO_4 does not lead to formation of appreciable amounts of a 1° carbocation. However, when the 3° alcohol is added, it is rapidly converted to a 3° carbocation, which then reacts with the 1° alcohol that is present in the mixture.

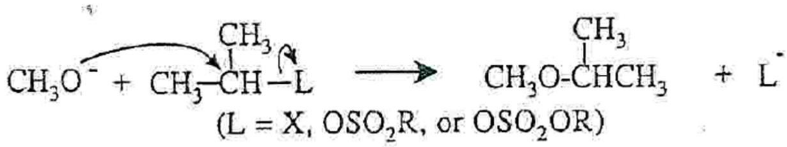
(a) Williamson senteziyle izopropil metil eter elde edilmesine ilişkin iki yöntem tasarlayınız. (b) Bu yöntemlerden birisi çok daha yüksek verimle eter elde edilmesini sağlar. Bunlardan hangisinin daha iyi yöntem olduğunu belirtiniz ve nedenini açıklayınız. ◀ **Problem 11.19**

11.19 (a) (1)



$$\mathrm{CH_3\overset{CH_3}{CH}O^-\,Na^+} + \mathrm{CH_3{-}L} \longrightarrow \mathrm{CH_3\overset{CH_3}{CH}O{-}CH_3} + \mathrm{L^-} + \mathrm{Na^+}$$
$$(\mathrm{L = X,\ OSO_2R,\ or\ OSO_2OR})$$

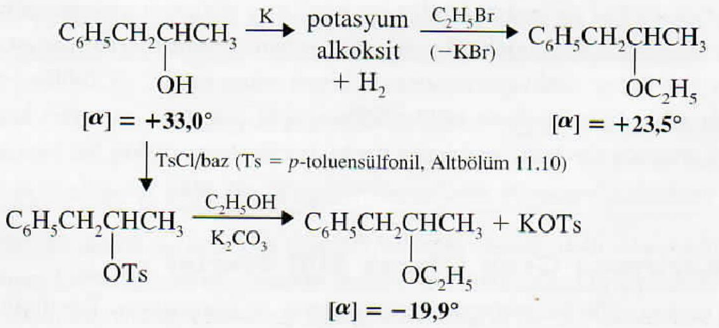
(2)



$$\mathrm{CH_3O^-} + \mathrm{CH_3{-}\overset{CH_3}{CH}{-}L} \longrightarrow \mathrm{CH_3O\text{-}\overset{CH_3}{CH}CH_3} + \mathrm{L^-}$$
$$(\mathrm{L = X,\ OSO_2R,\ or\ OSO_2OR})$$

(b) Both methods involve S_N2 reactions. Therefore, method (1) is better because substitution takes place at an unhindered methyl carbon atom. In method (2) where substitution must take place at a relatively hindered secondary carbon atom, the reaction would be accompanied by considerable elimination.

Problem 11.20 ◄ 2-Etoksi-1-fenilpropanın aşağıda gösterilen iki ayrı sentezi, optik çevirmeleri zıt olan ürünler verir.



$$C_6H_5CH_2\underset{\text{OH}}{\underset{|}{C}}HCH_3 \xrightarrow{K} \text{potasyum alkoksit} + H_2 \xrightarrow[(-KBr)]{C_2H_5Br} C_6H_5CH_2\underset{OC_2H_5}{\underset{|}{C}}HCH_3$$

$[\alpha] = +33{,}0°$ $\qquad$ $[\alpha] = +23{,}5°$

$\downarrow$ TsCl/baz (Ts = *p*-toluensülfonil, Altbölüm 11.10)

$$C_6H_5CH_2\underset{\text{OTs}}{\underset{|}{C}}HCH_3 \xrightarrow[K_2CO_3]{C_2H_5OH} C_6H_5CH_2\underset{OC_2H_5}{\underset{|}{C}}HCH_3 + KOTs$$

$[\alpha] = -19{,}9°$

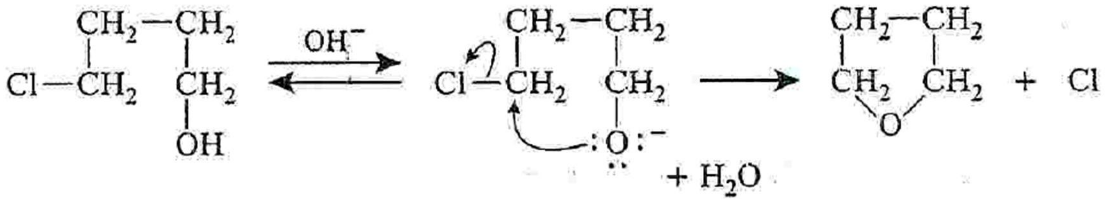
Bu sonucu nasıl açıklarsınız?

11.20 Reaction of the alcohol with K and then of the resulting salt with C_2H_5Br does not break bonds to the stereocenter, and these reactions therefore occur with retention of configuration at the stereocenter.

Reaction of the tosylate, $C_6H_5CH_2\underset{\text{OTs}}{\underset{|}{C}}HCH_3$, with C_2H_5OH in K_2CO_3 solution, however, is an S_N2 reaction that takes place at the stereocenter and thus it occurs with inversion at the stereocenter.

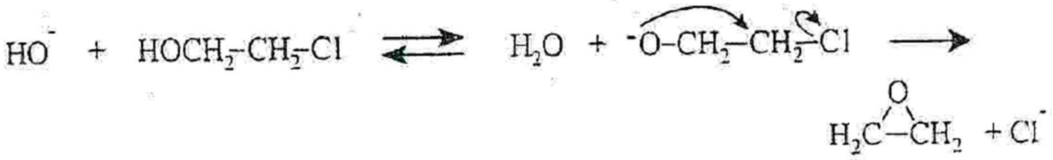
Problem 11.21 ➤ 4-Kloro-1-bütanol ve sulu sodyum hidroksitin tepkimesinden tetrahidrofuranın (THF) oluşumunun mekanizmasını yazınız.

11.21



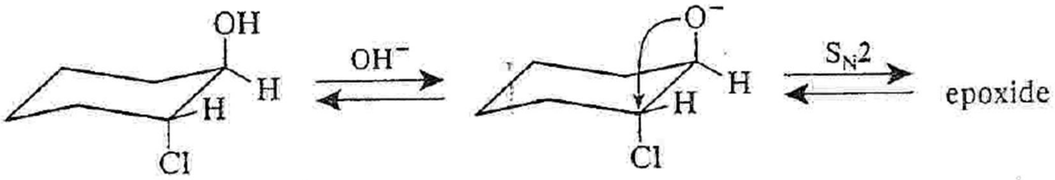
Problem 11.22 ➤ Epoksitler, halohidrinlerin sulu bazla tepkimesinden elde edilebilirler. Örneğin $ClCH_2CH_2OH$ ile sodyum hidroksit çözeltisinin etkileştirilmesinden etilen oksit elde edilir. (a) Bu tepkime için bir mekanizma öneriniz. (b) *trans*-2-Klorosikloheksanol, sodyum hidroksitle hemen tepkimeye girerek, siklohekseen oksiti oluşturur. *cis*-2-Klorosikloheksanol ise tepkime vermez. Bu farkı nasıl açıklarsınız?

11.22 (a)



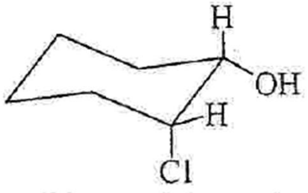
$$HO^- + HOCH_2{-}CH_2{-}Cl \rightleftharpoons H_2O + {}^-O{-}CH_2{-}CH_2{-}Cl \longrightarrow H_2C{-}CH_2\,(O) + Cl^-$$

(b) The $-\ddot{\underset{..}{O}}:^-$ group must displace the Cl^- from the backside,



trans-2-Chlorocyclohexanol

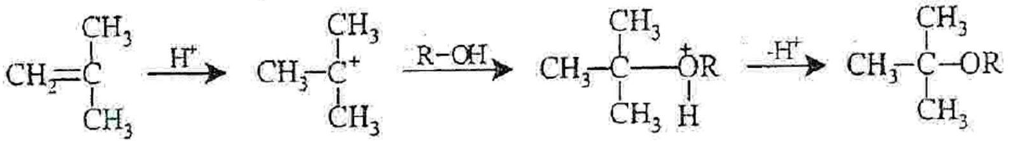
Backside attack is not possible with the cis isomer (below); therefore, it does not form an epoxide.



cis-2-Chlorocyclohexanol

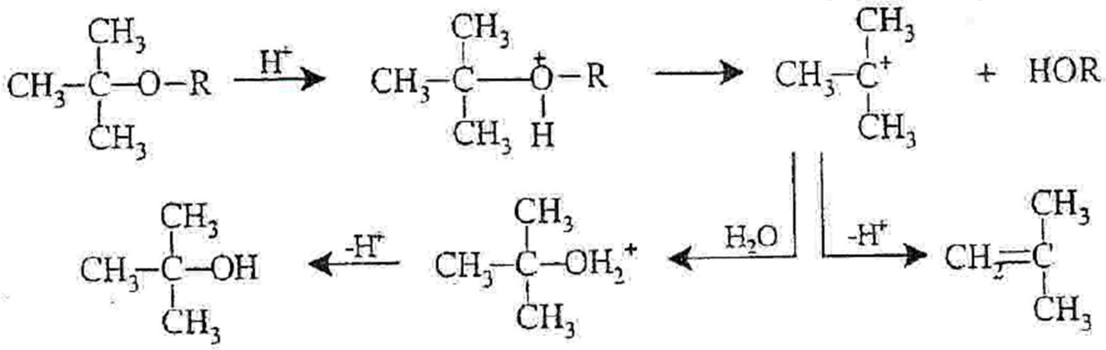
Problem 11.23 ➤ (a) Bir birincil alkol ve izobütilenden *ter*-bütil eter oluşumu mekanizması, Problem 11.18'de tartışılana benzemektedir. Bir mekanizma öneriniz. (b) Koruyucu ter-bütil grubunun çok kolay uzaklaştırılmasına etkiyen etken nedir? (Altbölüm 11.16'da da görüleceği gibi, diğer eterlerin bölünebilmesi için çok daha zorlayıcı koşullar gerekir.) (c) Koruyucu *ter*-bütil grubunun uzaklaştırılmasına ilişkin bir mekanizma öneriniz.

11.23 (a)



(b) The *tert*-butyl group is easily removed because, in acid, it is easily converted to a relatively stable, tertiary carbocation.

(c)

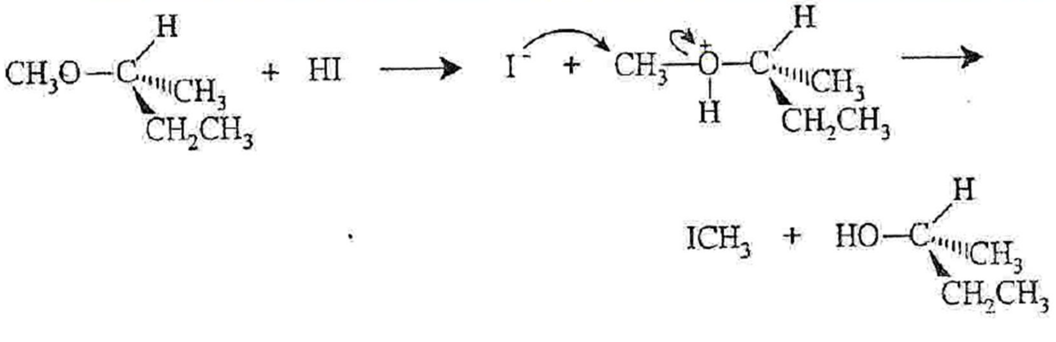


Problem 11.24 ➤ Bir eter, soğuk derişik HI ile etkileştirildiğinde, aşağıdaki gibi bir bölünme olur.

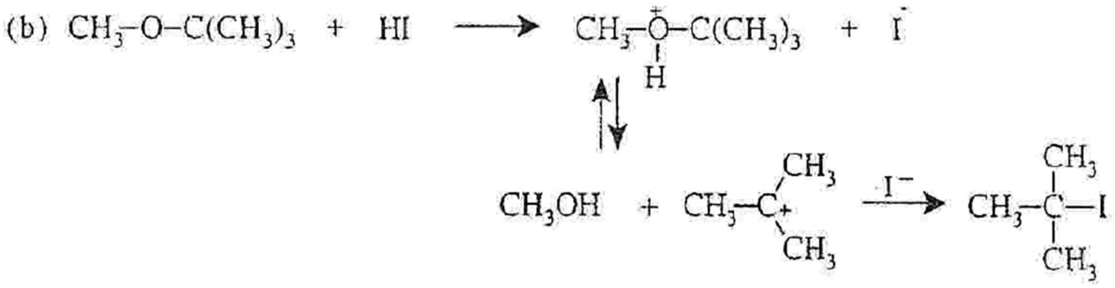
$$R{-}O{-}R + HI \longrightarrow ROH + RI$$

Karışık eterler kullanıldığında, oluşan alkol ve alkil halojenür, alkil gruplarının özelliğine bağlıdır. Aşağıdaki gözlemleri açıklayınız. (a) (*R*)-2-Metoksibütan tepkimeye girdiğinde, ürünler metil iyodür ve (*R*)-2-bütanoldür. (b) *ter*-Bütil metil eter tepkimeye girdiğindeyse ürünler metanol ve *ter*-bütil iyodürdür.

11.24 (a)



S_N2 attack of I^- occurs at the methyl carbon atom because it is less hindered; therefore, the bond between the *sec*-butyl group and the oxygen is not broken.



In this reaction the much more stable *tert*-butyl cation is produced. It then combines with I^- to form *tert*-butyl iodide.

Aşağıdaki her bir ürün için bir yapı öneriniz. **Problem 11.25**

(a) Oksiran $\xrightarrow[CH_3OH]{HA}$ $C_3H_8O_2$ (Metil Sellosolv olarak bilinen bir endüstriyel çözücü)

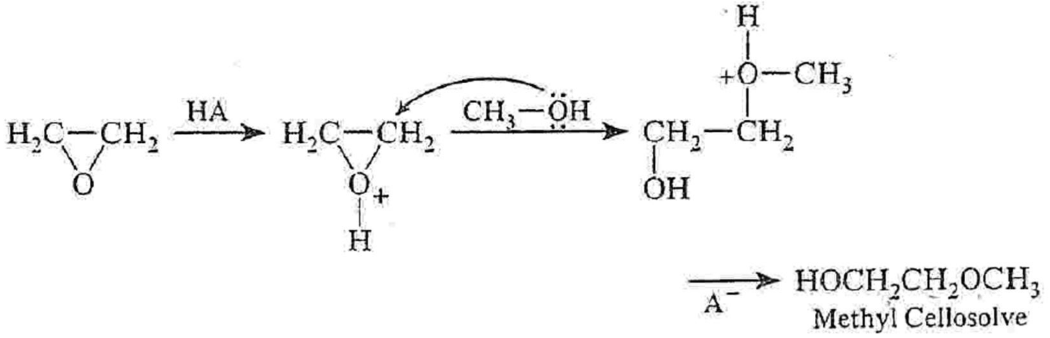
(b) Oksiran $\xrightarrow[CH_3CH_2OH]{HA}$ $C_4H_{10}O_2$ (Etil Sellosolv)

(c) Oksiran $\xrightarrow[H_2O]{KI}$ C_2H_4IO

(d) Oksiran $\xrightarrow{NH_3}$ C_2H_7NO

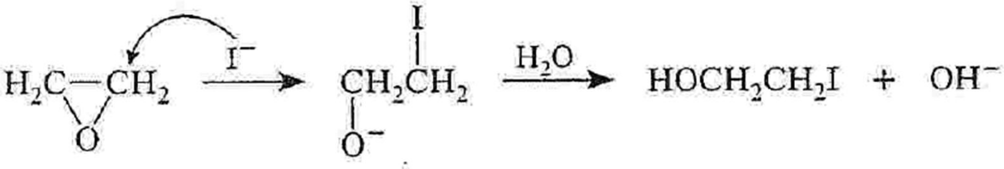
(e) Oksiran $\xrightarrow[CH_3OH]{CH_3}$ $C_3H_8O_2$

11.25 (a)

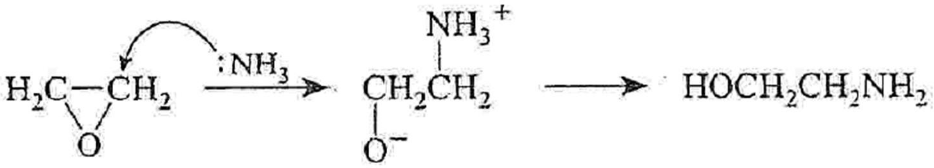


(b) An analogous reaction yields ethyl cellosolve, $HOCH_2CH_2OCH_2CH_3$.

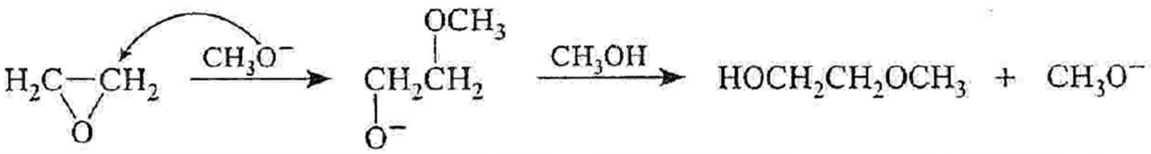
(c)



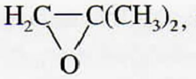
(d)



(e)

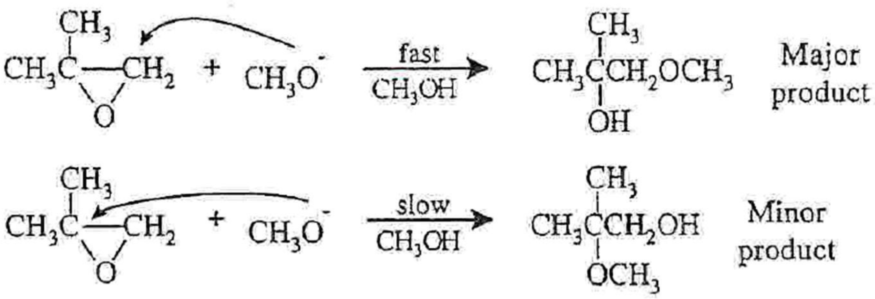


Problem 11.26 ➤ 2,2-Dimetiloksiran,

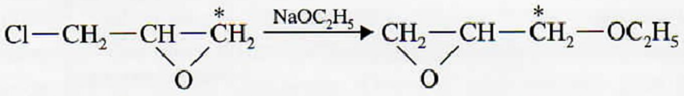


metanolde sodyum metoksitle etkileştirildiğinde başlıca 1-metoksi-2-metil-2-propanol verir. Bu sonucu nasıl açıklarsınız?

11.26 The reaction is an S_N2 reaction, and thus nucleophilic attack takes place much more rapidly at the primary carbon atom than at the more hindered secondary carbon atom.



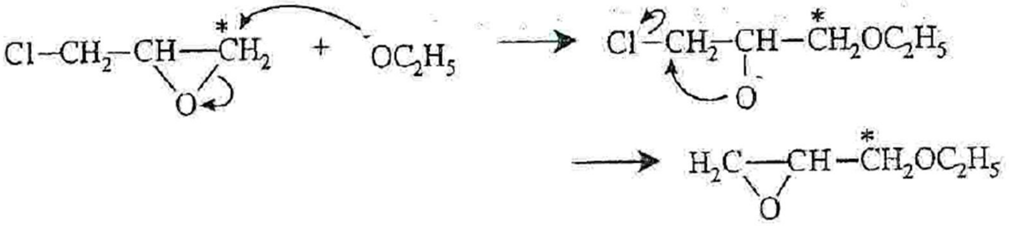
Problem 11.27 ➤ Sodyum etoksit, I'de yıldızla gösterilen ^{14}C ile etiketlenmiş 1-(klorometil)oksiranla tepkimeye girdiğinde, ana ürün, II'deki gibi etiketi taşıyan bir epoksittir. Bu tepkime için bir açıklama getiriniz.



I
1-(Klorometil)oksiran
(epiklorohidrin)

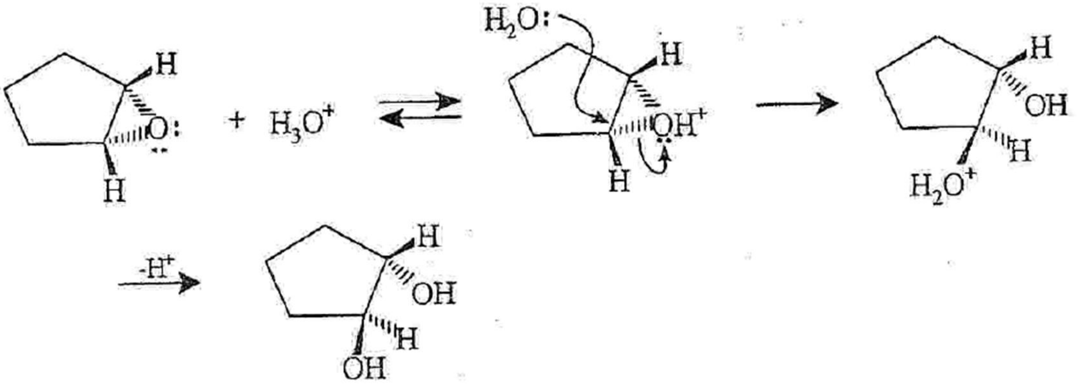
II

11.27 Ethoxide ion attacks the epoxide ring at the primary carbon because it is less hindered, and the following reactions take place.



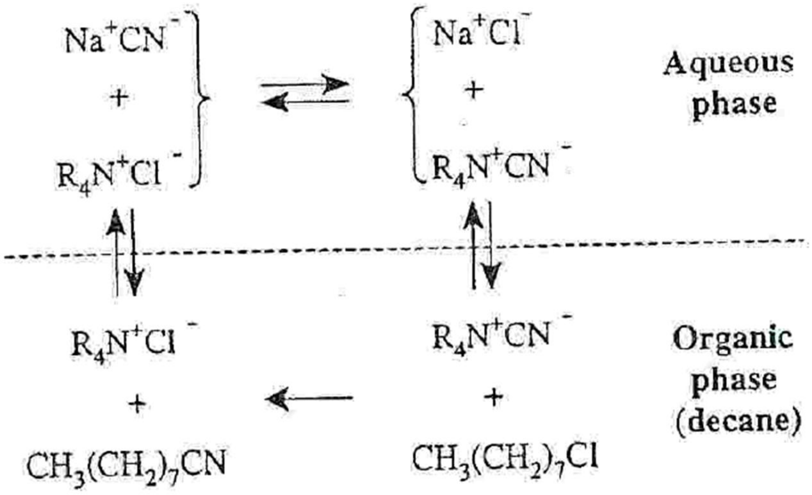
Problem 11.13 ➤ *trans*-1,2-Siklopentandiolün enantiyomerik şeklinin nasıl meydana geldiğini gösteren, daha önce verilmiş mekanizmaya benzer, bir mekanizma tasarlayınız.

11.28



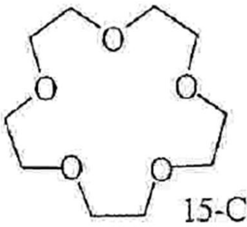
Şekil 11.5'te gösterildiği gibi $CH_3(CH_2)_6CH_2Cl$ ile siyanür iyonunun faz transfer katalizli tepkimesinin nasıl meydana geldiğini gösteren bir şema düzenleyiniz. Organik fazda hangi iyonun, su fazında hangi iyonunun bulunduğunu ve hangisinin bir fazdan diğerine geçtiğini gösterirken emin olunuz. ◄ **Problem 11.29**

11.29



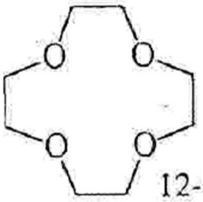
Problem 11.30 ➤ (a) 15-crown-5 ve (b) 12-crown-4'ün yapılarını yazınız.

11.30 (a)



15-Crown-5

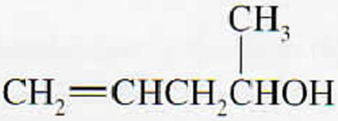
(b)



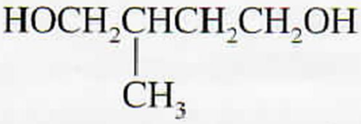
12-Crown-4

11.31 Aşağıdaki alkollerin IUPAC adlarını yazınız.

(a) $(CH_3)_3CCH_2CH_2OH$

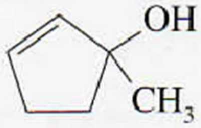
(b) 

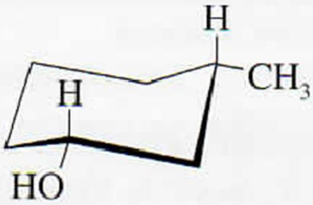
$CH_2{=}CHCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HOH$

(c) 

$HOCH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2OH$

(d) $C_6H_5CH_2CH_2OH$

(e) 

(f) 

11.31 (a) 3,3-Dimethyl-1-butanol

(b) 4-Penten-2-ol

(c) 2-Methyl-1,4-butanediol

(d) 2-Phenylethanol

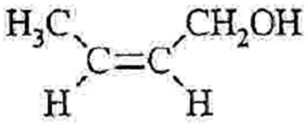
(e) 1-Methyl-2-cyclopenten-1-ol

(f) *cis*-3-Methylcyclohexanol

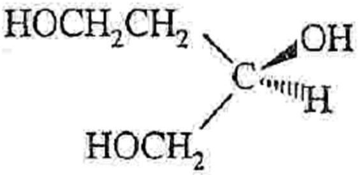
11.32 Aşağıda verilenlerin her birinin yapı formüllerini yazınız.

(a) (*Z*)-2-Büten-1-ol	(f) Tetrahidrofrun
(b) (*R*)-1,2,4-Bütantriol	(g) 2-Etoksipentan
(c) (1*R*,2*R*)-1,2-Siklopentandiol	(h) Etil fenil eter
(d) 1-Etilsiklobütanol	(i) Diizopropil eter
(e) 2-Kloro-3-heksin-1-ol	(j) 2-Etoksietanol

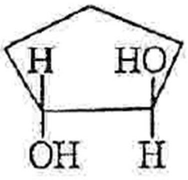
11.32 (a)



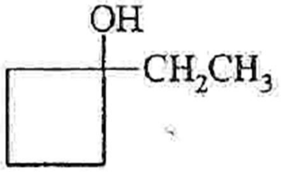
(b)



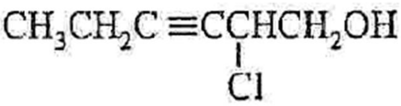
(c)



(d)

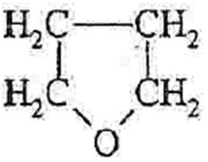


(e)

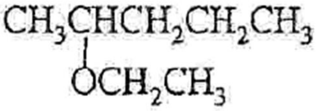


$CH_3CH_2C{\equiv}C\underset{Cl}{\underset{|}{C}}HCH_2OH$

(f)

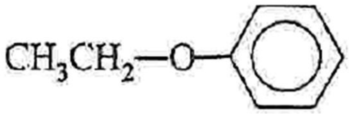


(g)

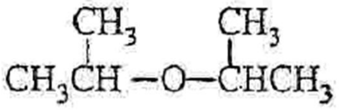


$CH_3\underset{OCH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

(h)



(i)



$CH_3\overset{CH_3}{\overset{|}{C}}H{-}O{-}\overset{CH_3}{\overset{|}{C}}HCH_3$

(j) $CH_3CH_2{-}O{-}CH_2CH_2OH$

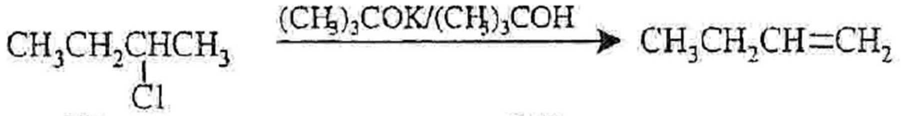
11.33 Aşağıda verilenlerin her birinden başlayarak 1-bütanolun en kolay yoldan sentezini tasarlayınız.

(a) 1-Büten (b) 1-Klorobütan (c) 2-Klorobütan (d) 1-Bütin

11.33 (a) $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(hydroboration)}]{THF:BH_3} (CH_3CH_2CH_2CH_2)_3B$

$\xrightarrow[\text{(oxidation)}]{H_2O_2/OH^-} CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CH_2Cl \xrightarrow{OH^-} CH_3CH_2CH_2CH_2OH$

(c) 

$\underset{\displaystyle Cl}{CH_3CH_2CHCH_3} \xrightarrow{(CH_3)_3COK/(CH_3)_3COH} CH_3CH_2CH{=}CH_2$

$\xrightarrow[ROOR]{HBr} CH_3CH_2CH_2CH_2Br \xrightarrow{OH^-} CH_3CH_2CH_2CH_2OH$

(d) $CH_3CH_2C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} CH_3CH_2CH{=}CH_2$

$\xrightarrow{\text{[as in (a)]}} CH_3CH_2CH_2CH_2OH$

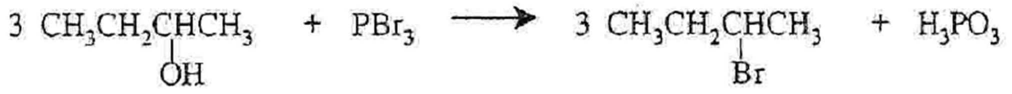
11.34 1-Bromobütanın aşağıda verilenlerden nasıl elde edebileceğinizi gösteriniz.

(a) 2-Bütanol, $CH_3CH_2CHOCH_3$

(b) 1-Bütanol, $CH_3CH_2CH_2CH_2OH$

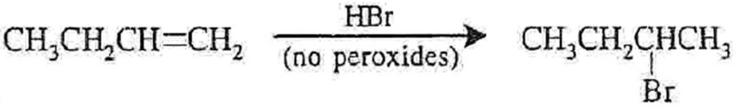
(c) 1-Büten

(d) 1-Bütin

11.34 (a) 

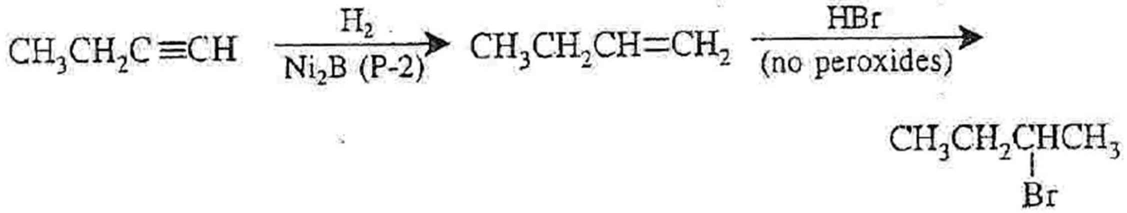
$3\ \underset{\displaystyle OH}{CH_3CH_2CHCH_3} + PBr_3 \longrightarrow 3\ \underset{\displaystyle Br}{CH_3CH_2CHCH_3} + H_3PO_3$

(b) $CH_3CH_2CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK}$



$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(no peroxides)}]{HBr} \underset{\displaystyle Br}{CH_3CH_2CHCH_3}$

(c) See (b) above.

(d) 

$CH_3CH_2C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(no peroxides)}]{HBr}$

$\underset{\displaystyle Br}{CH_3CH_2CHCH_3}$

11.35 Aşağıdaki dönüşümleri nasıl yapabileceğinizi gösteriniz.

(a) Sikloheksanol ⟶ klorosikloheksan

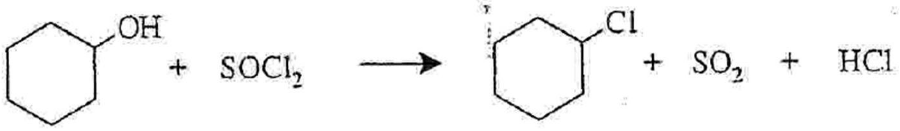
(b) Sikloheksen ⟶ klorosikloheksan

(c) 1-Metilsikloheksen ⟶ 1-bromo-1-metil-sikloheksan

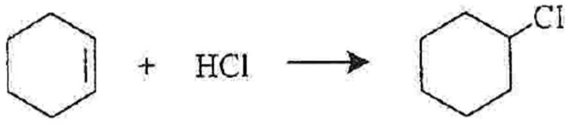
(d) 1-Metilsikloheksen ⟶ *trans*-2-metilsikloheksanol

(e) 1-Bromo-1-metilsikloheksan ⟶ sikloheksilmetanol

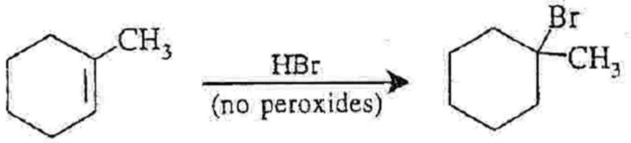
11.35 (a)



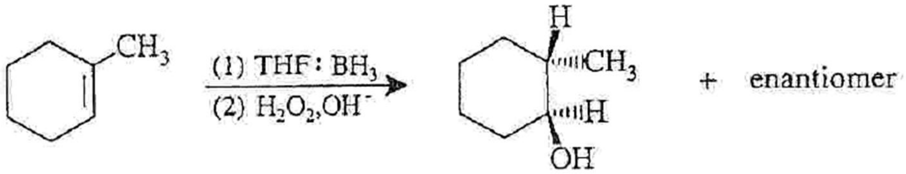
(b)



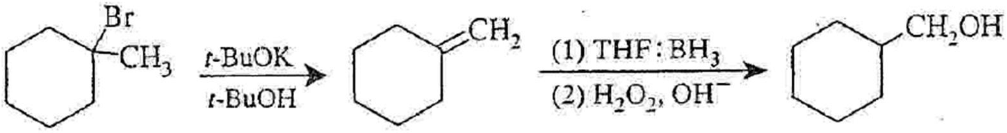
(c)



(d)

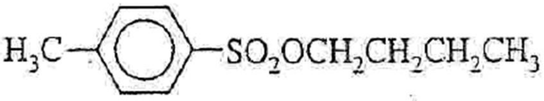
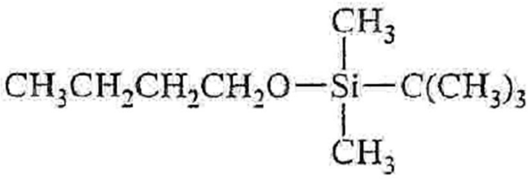


(e)

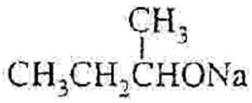
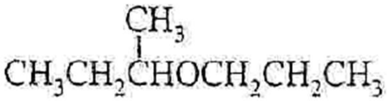
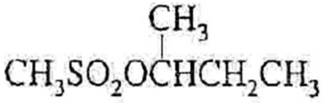
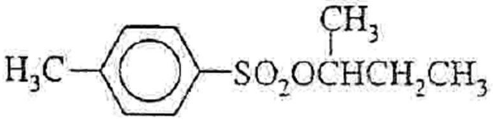


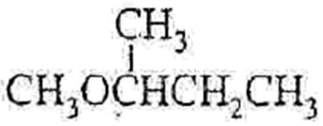
11.36 1-Bütanolün aşağıdaki reaktiflerin her biriyle etkileştirilmesi sonucunda oluşacak bileşiklerin yapılarını ve kabul edilebilir adlarını yazınız.

(a) Sodyum hidrür
(b) Sodyum hidrür, daha sonra 1-bromopropan
(c) Metansülfonil klorür ve baz
(d) *p*-Toluen sülfonil klorür
(e) (c) ürünü, sonra sodyum metoksit
(f) (d) ürünü, sonra KI
(g) Fosfor triklorür
(h) Tiyonil klorür
(i) Sülfürik asit, 140° C'da
(j) Derişik HBr ile geri soğutucu altında kaynatma
(k) *ter*-bütilklorodimetilsilan
(l) (k) ürünü, sonra florür iyonu

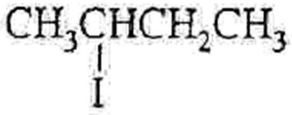
11.36	(a)	$CH_3CH_2CH_2CH_2ONa$	Sodium butoxide
	(b)	$CH_3CH_2CH_2CH_2OCH_2CH_2CH_3$	Butyl propyl ether
	(c)	$CH_3SO_2OCH_2CH_2CH_2CH_3$	Butyl mesylate
	(d)		Butyl tosylate
	(e)	$CH_3OCH_2CH_2CH_2CH_3$	1-Methoxybutane
	(f)	$CH_3CH_2CH_2CH_2I$	Butyl iodide
	(g)	$CH_3CH_2CH_2CH_2Cl$	Butyl chloride
	(h)	same as (g)	
	(i)	$CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$	Dibutyl ether
	(j)	$CH_3CH_2CH_2CH_2Br$	Butyl bromide
	(k)	 $CH_3CH_2CH_2CH_2O-\underset{CH_3}{\overset{CH_3}{Si}}-C(CH_3)_3$	Butyl *tert*-butyldimethylsilyl ether
	(l)	$CH_3CH_2CH_2CH_2OH$	1-Butanol

11.37 2-Bütanolün, Problem 11.36'da verilen reaktiflerin her biriyle etkileştirilmesiyle oluşabilecek bileşiklerin yapılarını ve adlarını yazınız.

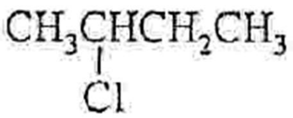
11.37	(a)	 $CH_3CH_2\overset{CH_3}{C}HONa$	Sodium *sec*-butoxide
	(b)	 $CH_3CH_2\overset{CH_3}{C}HOCH_2CH_2CH_3$	*sec*-Butyl propyl ether
	(c)	 $CH_3SO_2O\overset{CH_3}{C}HCH_2CH_3$	*sec*-Butyl mesylate
	(d)		*sec*-Butyl tosylate

(e) 
$CH_3OCH(CH_3)CH_2CH_3$

2-Methoxybutane

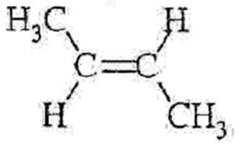
(f) 
$CH_3CH(I)CH_2CH_3$

sec-Butyl iodide

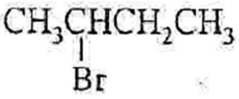
(g) 
$CH_3CH(Cl)CH_2CH_3$

sec-Butyl chloride

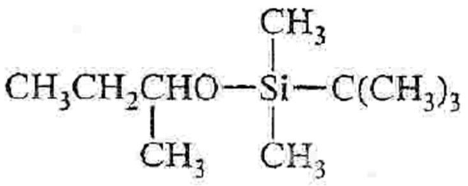
(h) same as (g)

(i) 

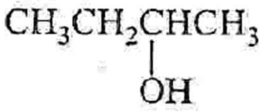
mainly, *trans*-2-Butene

(j) 
$CH_3CH(Br)CH_2CH_3$

sec-Butyl bromide

(k) 
$CH_3CH_2CH(CH_3)O{-}Si(CH_3)_2{-}C(CH_3)_3$

sec-Butyl *tert*-butyldimethylsilyl ether

(l) 
$CH_3CH_2CH(OH)CH_3$

2-Butanol

11.38 Aşağıdaki eterlerin her birinin aşırı, derişik hidrobromik asitle geri soğutucu altında kaynatılmasıyla hangi bileşiklerin oluşabileceğini belirtiniz.

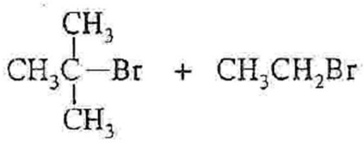
(a) Etil metil eter

(b) *ter*-Bütil etil eter

(c) Tetrahidrofuran

(d) 1,4-Dioksan

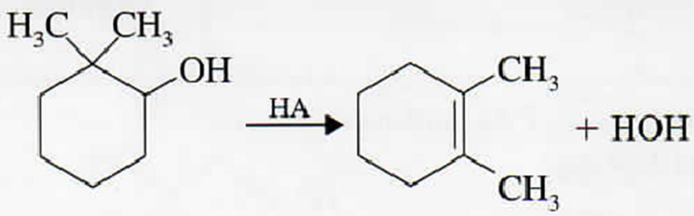
11.38 (a) $CH_3Br + CH_3CH_2Br$

(b) 
$CH_3C(CH_3)_2{-}Br + CH_3CH_2Br$

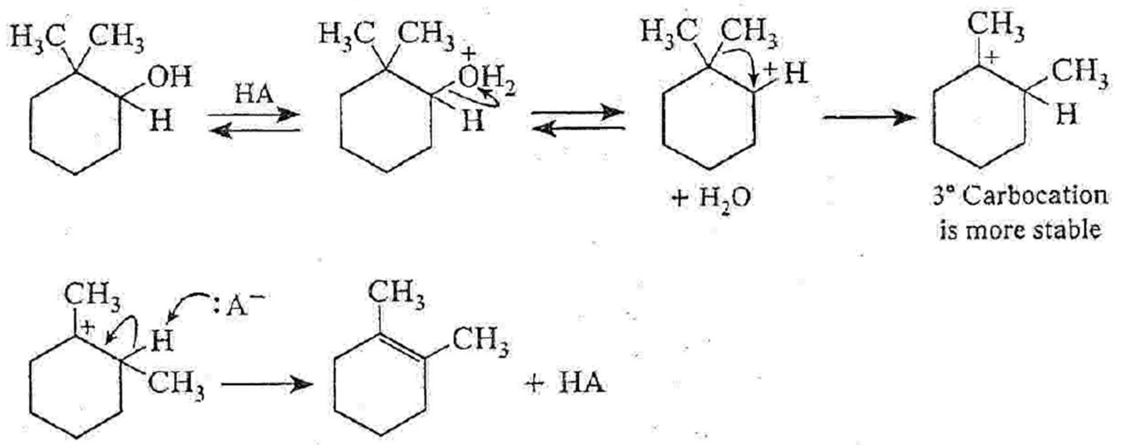
(c) $Br{-}CH_2CH_2CH_2CH_2{-}Br$

(d) $Br{-}CH_2CH_2{-}Br$ (2 molar equivalents)

11.39 Aşağıdaki tepkimeyi açıklayan bir mekanizma yazınız.



11.39



11.40 Aşağıdaki alkolleri elde etmek için, hidroborasyon-yükseltgeme işlemini nasıl uygulayabileceğinizi gösteriniz.

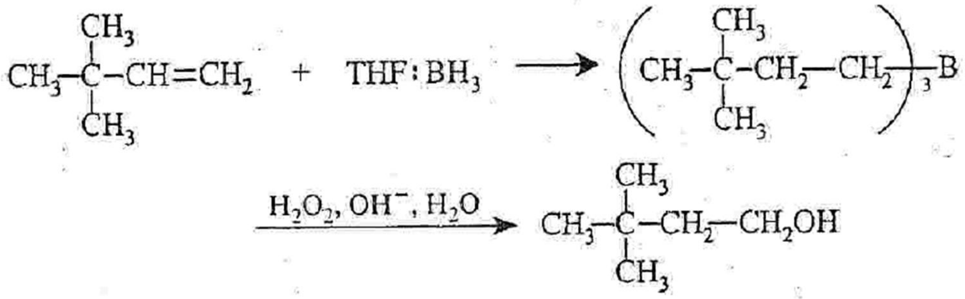
(a) 3,3-Dimetil-1-bütanol

(b) 1-Heksanol

(c) 2-Feniletanol

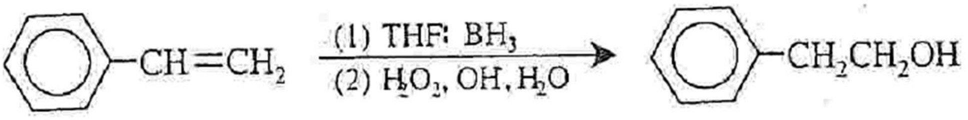
(d) *trans*-2-Metilsiklopentanol

11.40 (a)

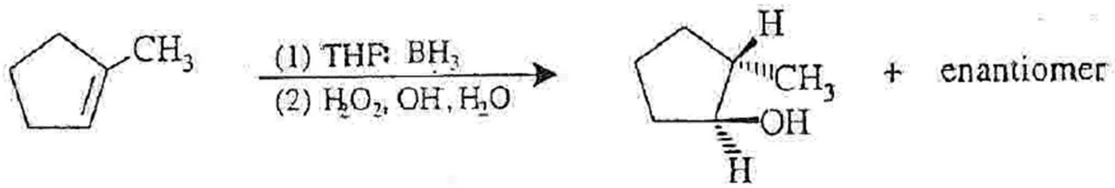


(b) $CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH^-,\ H_2O]{(1)\ THF{:}\ BH_3} CH_3CH_2CH_2CH_2CH_2CH_2OH$

(c)



(d)



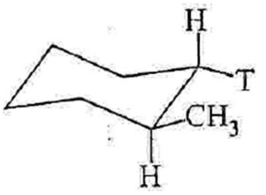
11.41 1-Metilsikloheksenin aşağıdaki reaktiflerin her biriyle etkileştirilmesi sonunda oluşacak ürünün üç boyutlu formülünü yazınız. Her bir üründeki, döteryum ve trityum atomlarının konumlarını gösteriniz.

(a) (1) THF: BH_3,(2)CH_3CO_2T

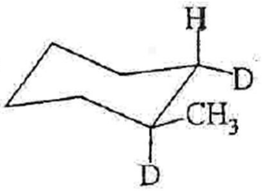
(b) (1) THF:BD_3, (2) CH_3CO_2D

(c) (1) THF:BD_3, (2) NaOH, H_2O_2, H_2O

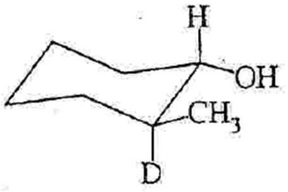
11.41 (a)



(b)

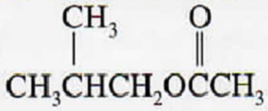


(c)



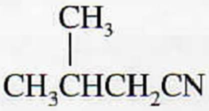
11.42 İzobütanla başlayarak aşağıdakilerin her birini nasıl sentezleyebileceğinizi gösteriniz (Problemin daha önceki şıklarında sentezi gösterilmiş bir bileşiği tekrar sentezlemenize gerek yoktur).

(a) *ter*-Bütil bromür
(b) 2-Metilpropen
(c) İzobütil bromür
(d) İzobütil iyodür
(e) İzobütil alkol (iki yoldan)
(f) *ter*-Bütil alkol
(g) İzobütil metil eter
(h)



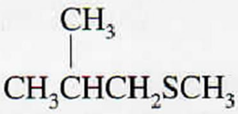
$CH_3\overset{CH_3}{C}HCH_2O\overset{O}{\overset{\|}{C}}CH_3$

(i)



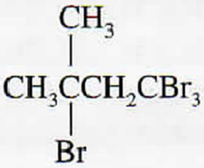
$CH_3\overset{CH_3}{C}HCH_2CN$

(j)



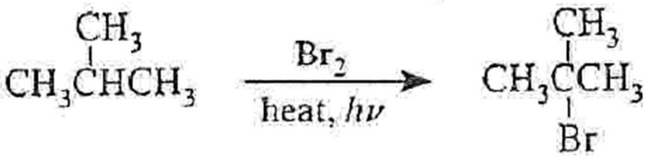
$CH_3\overset{CH_3}{C}HCH_2SCH_3$ (iki yoldan)

(k)



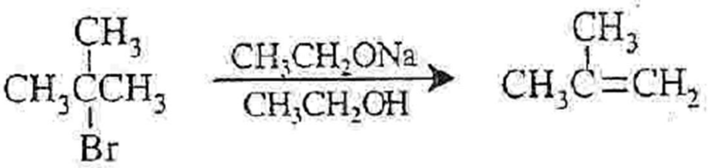
$CH_3\overset{CH_3}{\underset{Br}{C}}CH_2CBr_3$

11.42 (a)



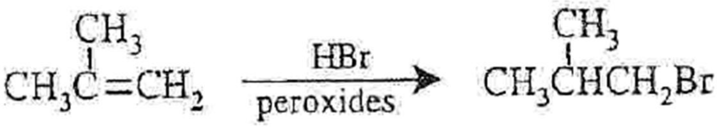
$$CH_3\overset{CH_3}{C}HCH_3 \xrightarrow[\text{heat, } h\nu]{Br_2} CH_3\overset{CH_3}{\underset{Br}{C}}CH_3$$

(b)



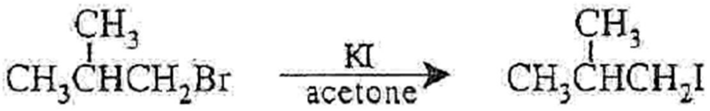
$$CH_3\overset{CH_3}{\underset{Br}{C}}CH_3 \xrightarrow[CH_3CH_2OH]{CH_3CH_2ONa} CH_3\overset{CH_3}{C}{=}CH_2$$

(c)



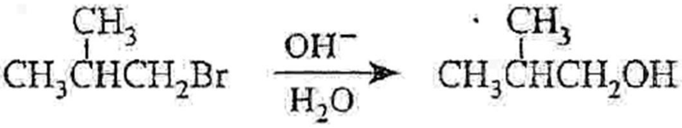
$$CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow[\text{peroxides}]{HBr} CH_3\overset{CH_3}{C}HCH_2Br$$

(d)



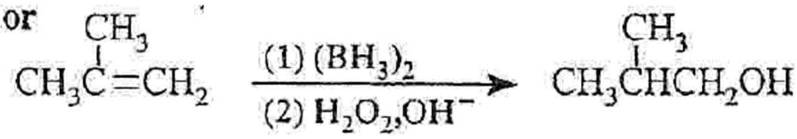
$$CH_3\overset{CH_3}{C}HCH_2Br \xrightarrow[\text{acetone}]{KI} CH_3\overset{CH_3}{C}HCH_2I$$

(e)



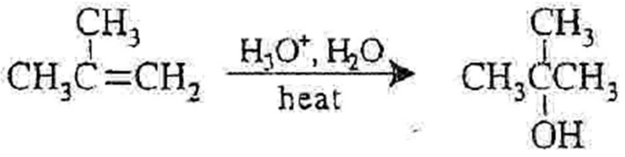
$$CH_3\overset{CH_3}{C}HCH_2Br \xrightarrow[H_2O]{OH^-} CH_3\overset{CH_3}{C}HCH_2OH$$

or

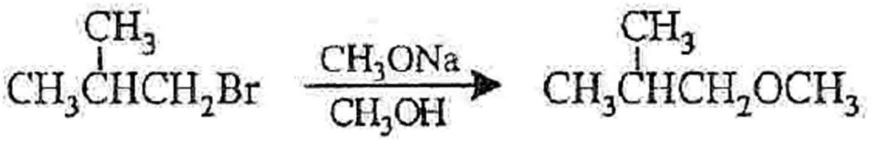


$$CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow[(2)\ H_2O_2, OH^-]{(1)\ (BH_3)_2} CH_3\overset{CH_3}{C}HCH_2OH$$

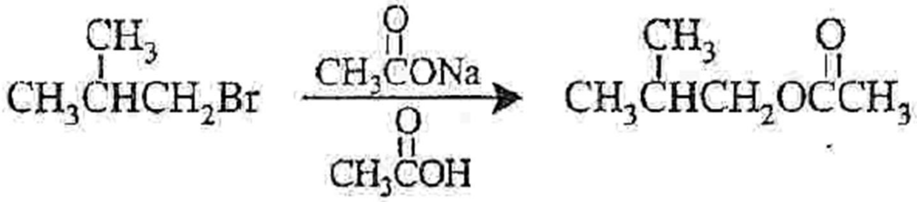
(f)



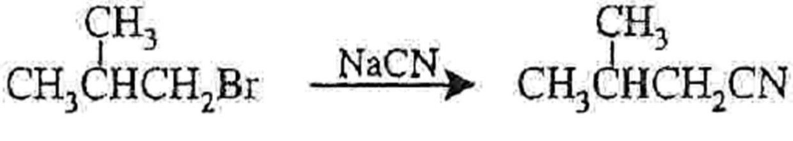
$$CH_3\overset{CH_3}{C}{=}CH_2 \xrightarrow[\text{heat}]{H_3O^+, H_2O} CH_3\overset{CH_3}{\underset{OH}{C}}CH_3$$

(g) 

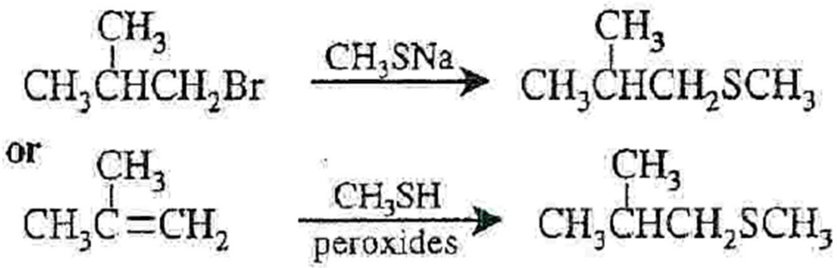
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br \xrightarrow[CH_3OH]{CH_3ONa} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OCH_3$$

(h) 

$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br \xrightarrow[CH_3\overset{O}{\overset{\|}{C}}OH]{CH_3\overset{O}{\overset{\|}{C}}ONa} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2O\overset{O}{\overset{\|}{C}}CH_3$$

(i) 

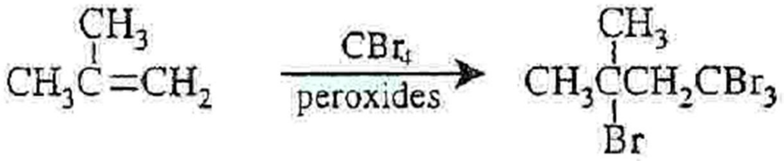
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br \xrightarrow{NaCN} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CN$$

(j) 

$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br \xrightarrow{CH_3SNa} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2SCH_3$$

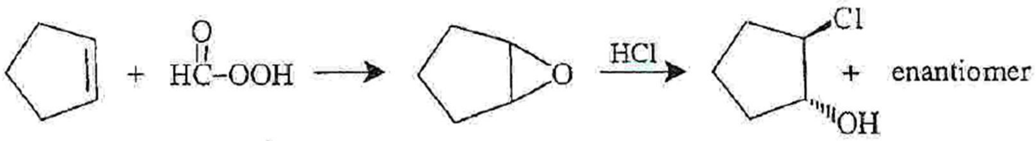
or

$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[peroxides]{CH_3SH} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2SCH_3$$

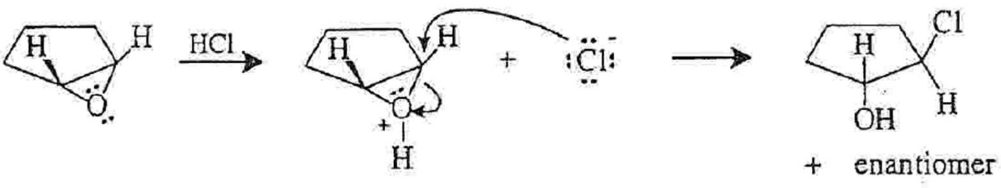
(k) 

$$CH_3\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[peroxides]{CBr_4} CH_3\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CBr_3$$

11.43 Komşu halo alkoller (halohidrinler), epoksitlerle HX'in etkileştirilmesiyle sentezlenebilirler. (a) Bu yöntemi, siklopentenden çıkarak 2-klorosiklopentanol sentezinde nasıl uygulayabileceğinizi gösteriniz. (b) Ürünün *cis*-2-klorosiklopentanol mü yoksa *trans*-2-klorosiklopentanol mü olmasını beklersiniz? Yani, —Cl ve —OH'nin net sin katılmasını mı yoksa net anti katılmasını mı beklersiniz? Açıklayınız.

11.43 (a) 

(b) The trans product because the Cl⁻ attacks anti to the epoxide and an inversion of configuration occurs.

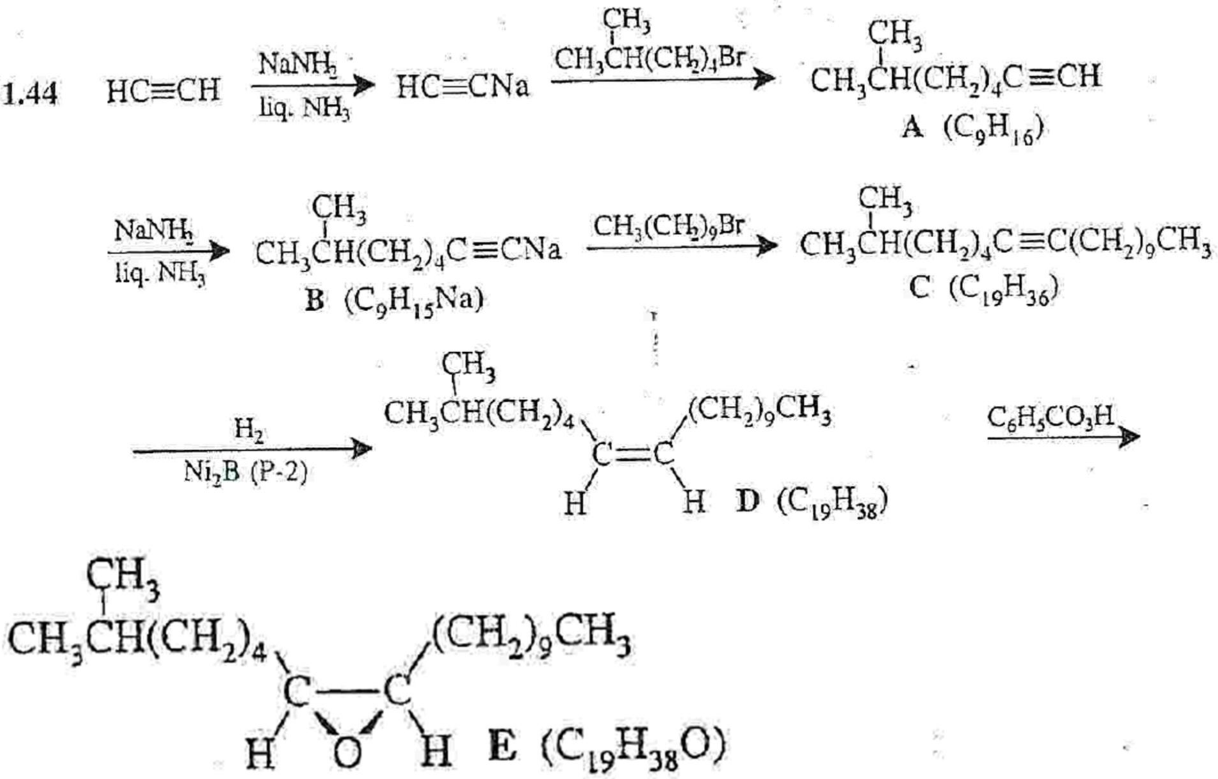


11.44 Güve seks çekicisi **E**'nin (bir tür feromon, bkz Altbölüm 4.16) bir sentezi aşağıda açıklanmıştır. Sentezdeki ara ürünlerin (**A–D**) ve **E**'nin yapısını gösteriniz.

$$HC\equiv CNa \xrightarrow[\text{sıvı } NH_3]{\text{1-bromo-5-metilheksan}} \mathbf{A}\ (C_9H_{16}) \xrightarrow[\text{sıvı } NH_3]{NaNH_2} \mathbf{B}\ (C_9H_{15}Na)$$

$$\xrightarrow{\text{1-bromodekan}} \mathbf{C}\ (C_{19}H_{36}) \xrightarrow[Ni_2B(P\text{-}2)]{H_2} \mathbf{D}\ (C_{19}H_{38}) \xrightarrow{C_6H_5CO_3H} \mathbf{E}\ (C_{19}H_{38}O)$$

11.44



$$HC\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} HC\equiv CNa \xrightarrow{CH_3\overset{CH_3}{C}H(CH_2)_4Br} CH_3\overset{CH_3}{C}H(CH_2)_4C\equiv CH \quad \mathbf{A}\ (C_9H_{16})$$

$$\xrightarrow[\text{liq. } NH_3]{NaNH_2} CH_3\overset{CH_3}{C}H(CH_2)_4C\equiv CNa \quad \mathbf{B}\ (C_9H_{15}Na) \xrightarrow{CH_3(CH_2)_9Br} CH_3\overset{CH_3}{C}H(CH_2)_4C\equiv C(CH_2)_9CH_3 \quad \mathbf{C}\ (C_{19}H_{36})$$

$$\xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} \mathbf{D}\ (C_{19}H_{38}) \xrightarrow{C_6H_5CO_3H} \mathbf{E}\ (C_{19}H_{38}O)$$

11.45 2-Metilpropenden (izobütilen) başlayarak ve gerekli diğer reaktifleri de kullanarak aşağıdaki her bir bileşiğin sentezini tasarlayınız.

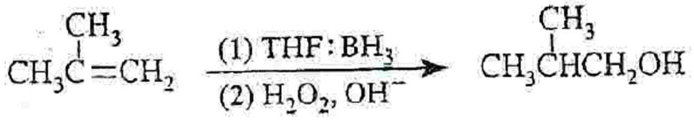
(a) $(CH_3)_2CHCH_2OH$

(b) $(CH_3)_2CHCH_2T$

(c) $(CH_3)_2CDCH_2T$

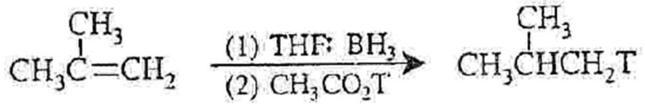
(d) $(CH_3)_2CHCH_2OCH_2CH_3$

11.45 (a)



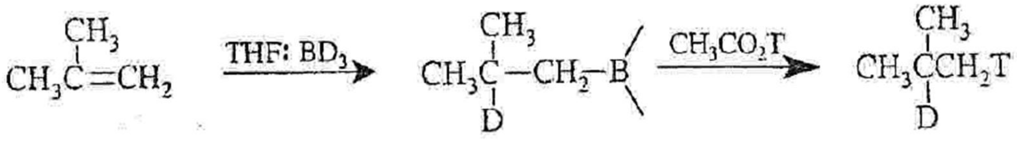
$$CH_3\overset{CH_3}{C}=CH_2 \xrightarrow[(2)\ H_2O_2,\ OH^-]{(1)\ THF:BH_3} CH_3\overset{CH_3}{C}HCH_2OH$$

(b)



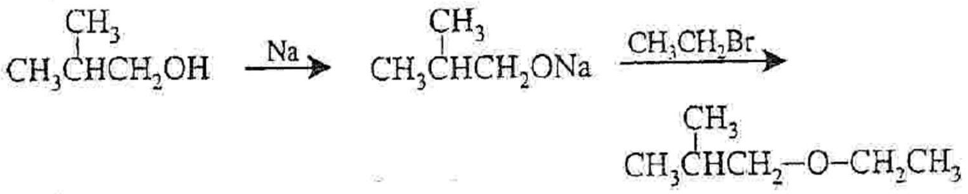
$$CH_3\overset{CH_3}{C}=CH_2 \xrightarrow[(2)\ CH_3CO_2T]{(1)\ THF:BH_3} CH_3\overset{CH_3}{C}HCH_2T$$

(c)



$$CH_3\overset{CH_3}{C}=CH_2 \xrightarrow{THF:BD_3} CH_3\overset{CH_3}{\underset{D}{C}}-CH_2-B\langle \xrightarrow{CH_3CO_2T} CH_3\overset{CH_3}{\underset{D}{C}}CH_2T$$

(d)



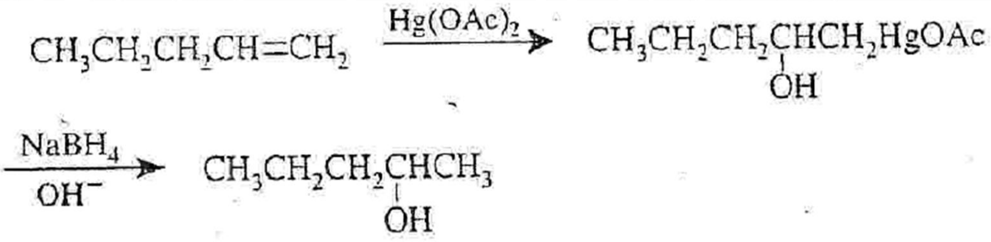
$$CH_3\overset{CH_3}{C}HCH_2OH \xrightarrow{Na} CH_3\overset{CH_3}{C}HCH_2ONa \xrightarrow{CH_3CH_2Br} CH_3\overset{CH_3}{C}HCH_2-O-CH_2CH_3$$

11.46 Aşağıda verilen alkolleri, uygun alkenlerden başlayarak oksiciva katılması–civa ayrılmasıyla nasıl elde edebileceğinizi gösteriniz.

(a) 2-Pentanol **(c)** 3-Metil-3-pentanol

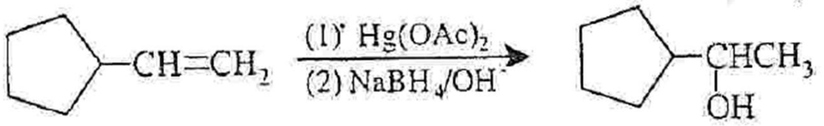
(b) 1-Siklopentiletanol **(d)** 1-Etilsiklopentanol

11.46 (a)

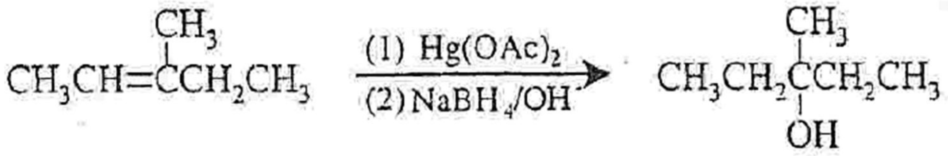


$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{Hg(OAc)_2} CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2HgOAc \xrightarrow[OH^-]{NaBH_4} CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

(b)

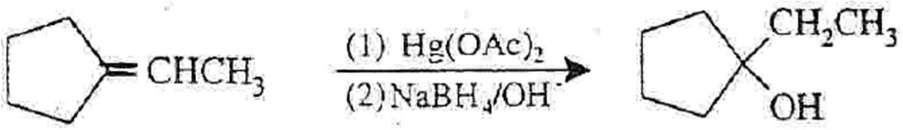


(c)



$$CH_3CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH_2CH_3 \xrightarrow[(2)\ NaBH_4/OH^-]{(1)\ Hg(OAc)_2} CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}CH_2CH_3$$

(d)



***11.47** **A–L** Bileşiklerinin her birinin stereokimyasal formülünü gösteriniz; (b) ve (g) şıklarındaki soruları cevaplayınız.

(a) 1-Metilsiklobüten $\xrightarrow[(2)\ H_2O_2, OH^-]{(1)\ THF: BH_3}$ **A** $(C_5H_{10}O)$ $\xrightarrow[OH^-]{TsCl}$ **B** $(C_{12}H_{16}SO_3)$ $\xrightarrow{OH^-}$ **C** $(C_5H_{10}O)$

(b) **A** ve **C** arasındaki stereoizomerik ilişki nedir?

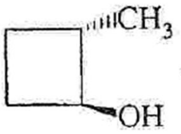
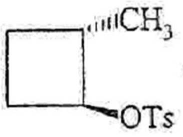
(c) **B** $(C_{12}H_{16}SO_3)$ $\xrightarrow{I^-}$ **D** (C_5H_9I)

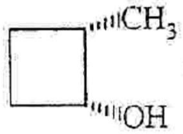
(d) *trans*-4-Metilsikloheksanol $\xrightarrow[OH^-]{MsCl}$ **E** $(C_8H_{16}SO_3)$ $\xrightarrow{HC{\equiv}CNa}$ **F** (C_9H_{14})

(e) (*R*)-2-Bütanol $\xrightarrow{NaH}$ [**H** (C_4H_9ONa)] $\xrightarrow{CH_3I}$ **J** $(C_5H_{12}O)$

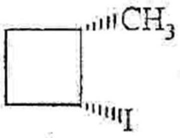
(f) (*R*)-2-Bütanol $\xrightarrow{MsCl}$ **K** $(C_5H_{12}SO_3)$ $\xrightarrow{CH_3ONa}$ **L** $(C_5H_{12}O)$

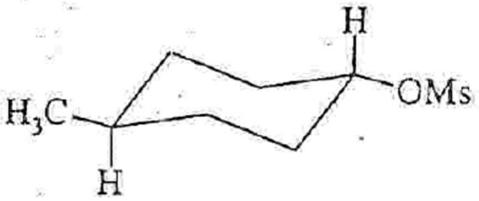
(g) **J** ve **L** arasındaki stereoizomerik ilişki nedir?

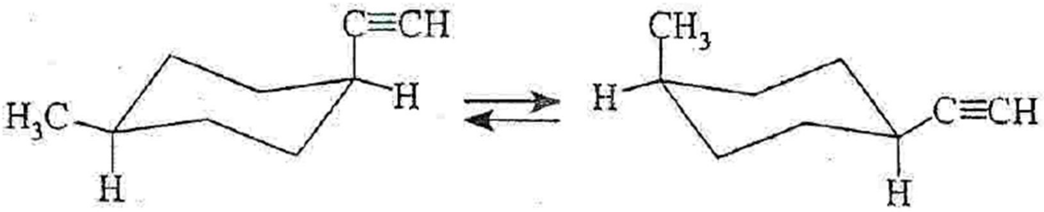
*11.47 (a) A =  + enantiomer B =  + enantiomer

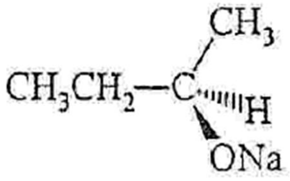
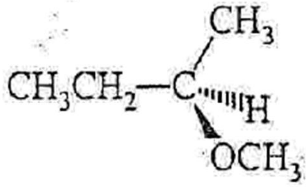
C =  + enantiomer

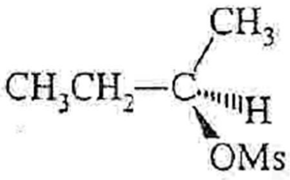
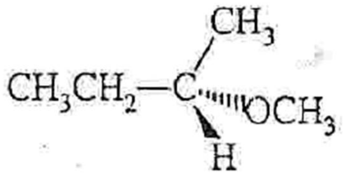
(b) Diastereomers

(c) D =  + enantiomer

(d) E = 

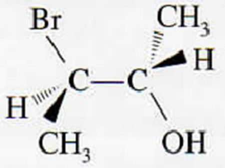
F = 

(e) H =  J = 

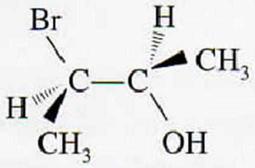
(f) K =  L = 

(g) Enantiomers

***11.48** Stereokimyasal yapısı **A** olan 3-bromo-2-bütanol derişik HBr ile etkileştirildiğinde *mezo*-2,3-dibromobütanı oluşturur; 3-bromo-2-bütanol, **B**, benzer tepkimeyle (±)-2,3-dibromobütanı meydana getirir. 1939 yılında S. Winstein ve H. J. Lucas tarafından gerçekleştirilen bu klasik deneme, **komşu grup etkileri** olarak adlandırılan araştırma serisinin başlangıç noktasıdır. Bu tepkimelerin stereokimyasını açıklayan mekanizmalar öneriniz.



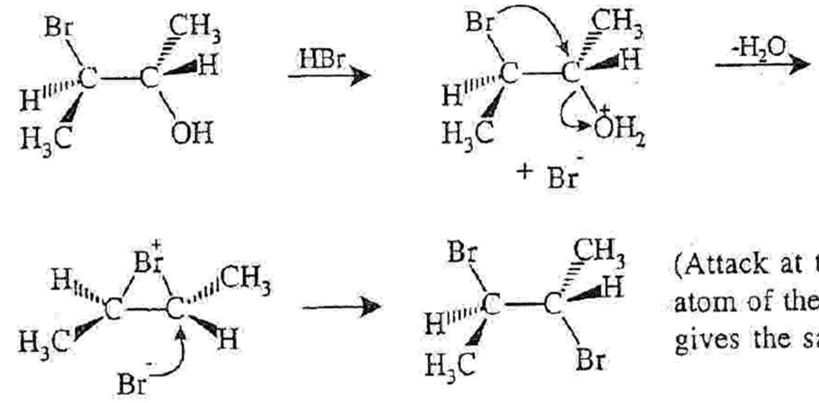
A



B

***11.48** The reactions proceed through the formation of bromonium ions identical to those formed in the bromination of *trans*- and *cis*-2-butene (see Section 8.7A).

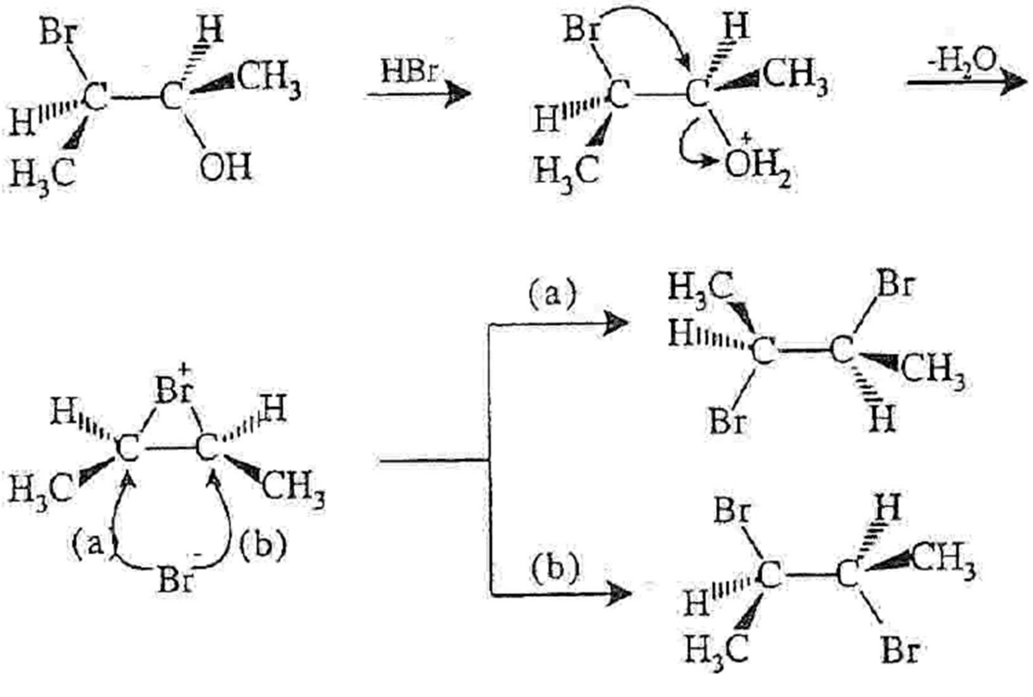
A



(Attack at the other carbon atom of the bromonium ion gives the same product.)

meso-2,3-Dibromobutane

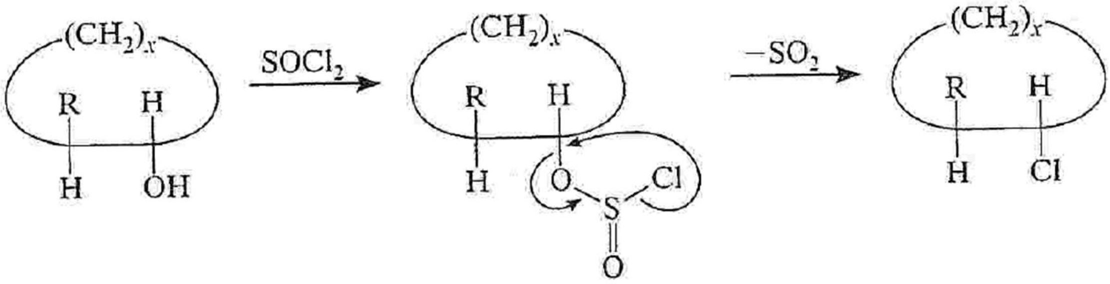
B



(±)-2,3-Dibromobutane

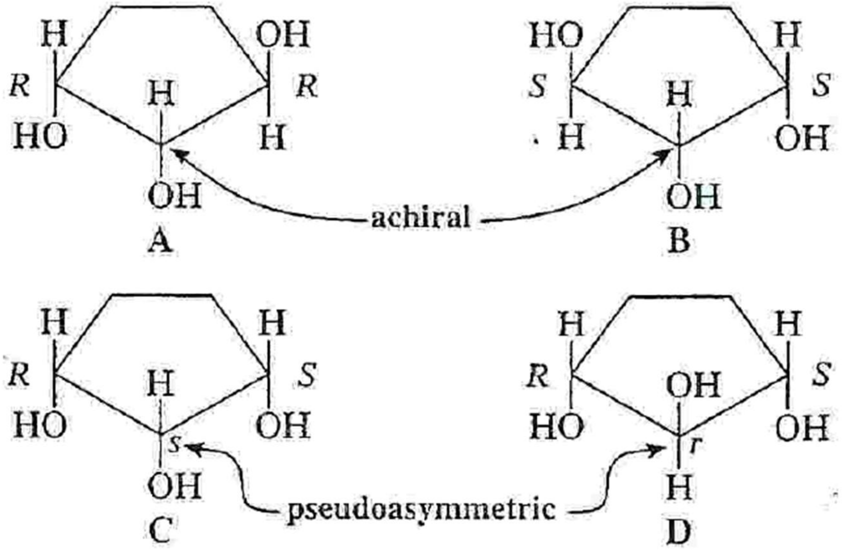
***11.49** Bir üçüncül amin (veya piridin) varlığında, bir alkolün tiyonil klorürle tepkimesi sonunda, OH grubunun, *konfigürasyonun devrilmesiyle* Cl ile yer değiştirmiş olduğu bir ürün meydana gelir (Altbölüm 11.14). Ancak amin olmadığında genellikle konfigurasyonun korunduğu bir yer değiştirme gerçekleşir. Her iki durumda da aynı klorosülfit ara ürünü oluşmaktadır. Bu ara ürünün, konfigürasyonun korunduğu ürünü oluşturmasına ilişkin bir mekanizma öneriniz.

*11.49



11.50 1,2,3-Siklopentantriol bileşiğinin olası stereoizomerlerini yazınız. Stereomerkezleri işaretleyiniz ve hangilerinin enantiyomer, hangilerinin diastereomer olduklarını belirtiniz. [Bazı izomerler "yalancı asimetrik merkez" içerirler; bunun iki konfigürasyonu mümkündür, her biri farklı bir izomer meydana getirir, bunların her biri ayna görüntüleriyle aynıdır. Bu gibi stereoizomerler sadece yalancıasimetrik merkeze bağlı ***R***, ***S*** gruplarının düzenlenme şekliyle farklandırılabilirler. Bunlardan ***R***, ***S***'den daha öncelikli kabul edilerek, konfigürasyon ***r*** ya da *s* olarak belirlenir. Yalancı asimetri belirlenmesinde küçük harfler kullanılır.]

*11.50



A and B are enantiomers

A, C, and D are all diastereomers

B, C, and D are all diastereomers

C is meso

D is meso

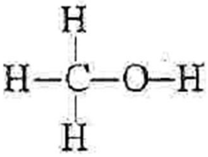
Alkollerin Karbonil Bileşiklerinden Sentezi. Yükseltgenme – İndirgenme ve Organometalik Bileşikler

Problem 12.1

Bir organik bileşiğin karbon atomunun yükseltgenme sayısı karbona bağlı gruplara bakılarak bulunabilir. Hidrojenle (veya karbondan daha az elektronegatif herhangi bir elementle) olan bir bağ, karbonun yükseltgenme sayısına –1; oksijen, azot veya halojenle (veya karbondan daha elektronegatif herhangi bir elementle) olan bir bağ karbonun yükseltgenme sayısına +1; başka bir karbonla olan bağ ise 0 etki yapar. Buna göre, metanda karbonun yükseltgenme durumu –4 ve karbon dioksitte +4'tür. (a) Bu yöntemi kullanarak, metanol (CH_3OH), formik asit $\left(\overset{O}{\overset{\|}{HCOH}}\right)$ ve formaldehitte $\left(\overset{O}{\overset{\|}{HCH}}\right)$ karbon atomlarının yükseltgenme durumunu tayin ediniz. (b) Metan, karbon dioksit, metanol, formik asit ve formaldehiti karbonun artan yükseltgenme durumuna göre sıralayınız. (c) Metanol ⟶ formaldehit tepkimesindeki yükseltgenme durumu değişmesi nedir? (d) Bu bir yükseltgenme mi yoksa indirgenme midir? (e) Bu tepkimede, yükseltgen olarak H_2CrO_4, kullanılırsa H_2CrO_4'teki krom Cr^{3+} haline gelir. Kromun yükseltgenme durumunda ne gibi bir değişiklik olmuştur?

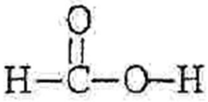
Yükseltgenme-indirg
tepkimelerinin denkl
mesi. Organik yüksel
me-indirgenme
tepkimelerinin eşitler
için, bu kitabın çalışı
klavuzunda bir yönte
açıklanmıştır.

12.1 (a)



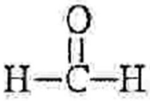
$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-O-H$$

3 H = -3
1 O = +1
Total = -2 = oxidation state of C



$$H-\overset{O}{\overset{\|}{C}}-O-H$$

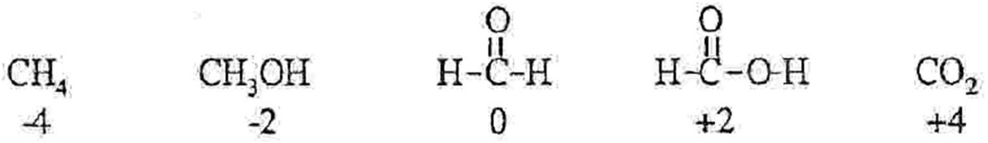
1 H = -1
3 O = +3
Total = +2 = oxidation state of C



$$H-\overset{O}{\overset{\|}{C}}-H$$

2 H = -2
2 O = +2
Total = 0 = oxidation state of C

(b)



CH_4	CH_3OH	$H-\overset{O}{\overset{\|}{C}}-H$	$H-\overset{O}{\overset{\|}{C}}-OH$	CO_2
-4	-2	0	+2	+4

(c) A change from −2 to 0

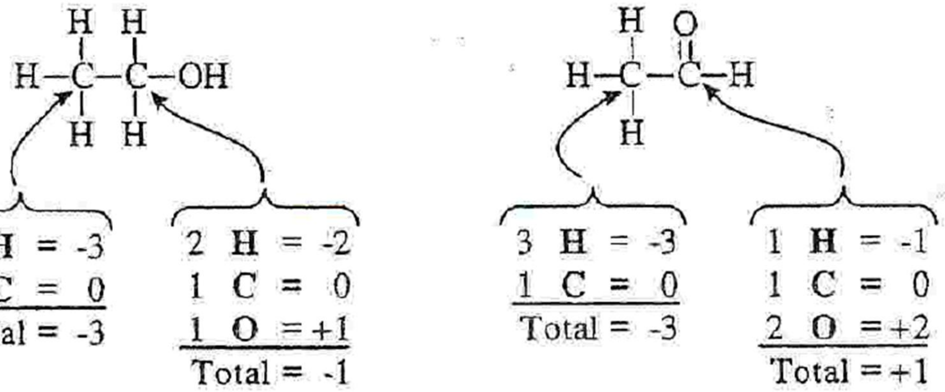
(d) An oxidation, since the oxidation state increases

(e) A reduction from +6 to +3

Problem 12.2

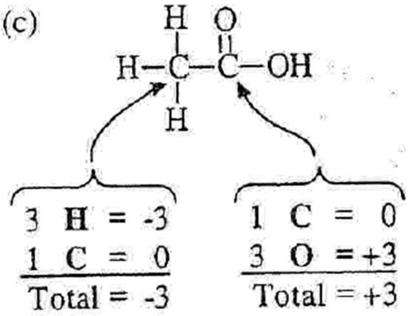
(a) Etanolün ve asetaldehitin her bir karbon atomunun yükseltgenme durumunu belirlemek için önceki problemde açıklanan yöntemi kullanınız. (b) Etanol asetaldehite yükseltgendiğinde bu sayılar yükseltgenme yeri konusunda ne ifade eder? (c) Bu işlemi, asetaldehitin asetik asite yükseltgenmesi için tekrarlayınız.

12.2 (a)



(b) Only the carbon atom of the $-CH_2OH$ group of ethanol undergoes a change in oxidation state. The oxidation state of the carbon atom in the CH_3- group remains unchanged.

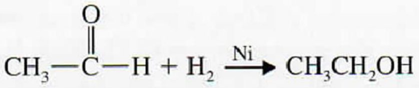
(c)



The oxygen-bearing carbon atom increases its oxidation state from +1 (in acetaldehyde) to +3 (in acetic acid).

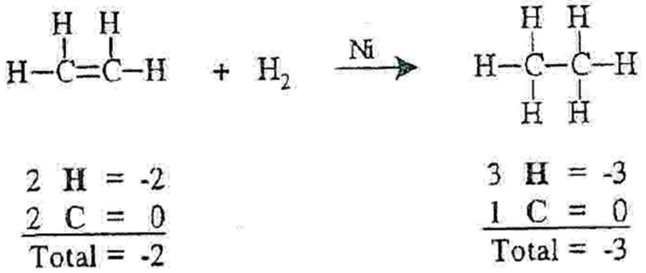
Problem 12.3

(a) Bir alkenin hidrojenlenmesini, bir katılma tepkimesi olarak açıklamamıza karşın, organik kimyacılar çoğu kez bunu bir "indirgeme" olarak ifade ederler. Problem 12.1'deki yöntemi göz önüne alarak bunu açıklayınız. (b) Benzer yorumları aşağıdaki tepkime için yapınız.



$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Ni} CH_3CH_2OH$$

12.3 (a) If we consider the hydrogenation of ethene as an example, we find that the oxidation state of carbon decreases. Thus, because the reaction involves the *addition* of *hydrogen*, it is both an *addition reaction* and a *reduction*.



(b) The hydrogenation of acetaldehyde is not only an addition reaction, but it is also a *reduction* because the carbon atom of the C=O group goes from a + 1 to a − 1 oxidation state. The reverse reaction (the *dehydrogenation* of ethanol) is not only an *elimination* reaction, but also an *oxidation*.

Ion-Electron Half-Reaction Method for Balancing Organic Oxidation–Reduction Equations

Only two simple rules are needed:

Rule 1 Electrons (e^-) together with protons (H^+) are arbitrarily considered the reducing agents in the half-reaction for the reduction of the oxidizing agent. Ion charges are balanced by *adding electrons to the left-hand side.* (If the reaction is run in neutral or basic solution, add an equal number of OH^- ions to both sides of the balanced half-reaction to neutralize the H^+, and show the resulting $H^+ + OH^-$ as H_2O.)

Rule 2 Water (H_2O) is arbitrarily taken as the formal source of oxygen for the oxidation of the organic compound, producing *product, protons,* and *electrons* on the right-hand side. (Again, use OH^- to neutralize H^+ in the *balanced* half-reaction in neutral or basic media.)

EXAMPLE 1

Write a balanced equation for the oxidation of RCH_2OH to RCO_2H by $Cr_2O_7^{2-}$ in acid solution.

Reduction half-reaction:

$$Cr_2O_7^{2-} + H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Balancing atoms and charges:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$$

Oxidation half-reaction:

$$RCH_2OH + H_2O = RCO_2H + 4H^+ + 4e^-$$

The least common multiple of a 6-electron uptake in the reduction step and a 4-electron loss in the oxidation step is 12, so we multiply the first half-reaction by 2 and the second by 3, and add:

$$3RCH_2OH + 3H_2O + 2Cr_2O_7^{2-} + 28H^+ = 3RCO_2H + 12H^+ + 4Cr^{3+} + 14H_2O$$

Canceling common terms, we get:

$$3RCH_2OH + 2Cr_2O_7^{2-} + 16H^+ = 3RCO_2H + 4Cr^{3+} + 11H_2O$$

This shows that the oxidation of 3 mol of a primary alcohol to a carboxylic acid requires 2 mol of dichromate.

EXAMPLE 2

Write a balanced equation for the oxidation of styrene to benzoate ion and carbonate ion by MnO_4^- in alkaline solution.

Reduction:

$$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O \text{ (in acid)}$$

Since this reaction is carried out in basic solution, we must add 4 OH^- to neutralize the $4H^+$ on the left side, and, of course, 4 OH^- to the right side to maintain a balanced equation.

$$MnO_4^- + 4H^+ + 4\,OH^- + 3e^- = MnO_2 + 2H_2O + 4\,OH^-$$

or, $MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4\,OH^-$

Oxidation:

$$ArCH{=}CH_2 + 5H_2O = ArCO_2^- + CO_3^{2-} + 13H^+ + 10e^-$$

We add 13 OH^- to each side to neutralize the H^+ on the right side,

$$ArCH{=}CH_2 + 5H_2O + 13\,OH^- = ArCO_2^- + CO_3^{2-} + 13H_2O + 10e^-$$

The least common multiple is 30, so we multiply the reduction half-reaction by 10 and the oxidation half-reaction by 3 and add:

$$3ArCH{=}CH_2 + 39\,OH^- + 10MnO_4^- + 20H_2O = 3ArCO_2^- + 3CO_3^{2-} + 24H_2O + 10MnO_2 + 40\,OH^-$$

Canceling:

$$3ArCH{=}CH_2 + 10MnO_4^- = 3ArCO_2^- + 3CO_3^{2-} + 4H_2O + 10MnO_2 + OH^-$$

SAMPLE PROBLEMS

Using the ion–electron half-reaction method, write balanced equations for the following oxidation reactions.

(a) Cyclohexene + $MnO_4^- + H^+ \xrightarrow{\text{(hot)}} HO_2C(CH_2)_4CO_2H + Mn^{2+} + H_2O$

(b) Cyclopentene + $MnO_4^- + H_2O \xrightarrow{\text{(cold)}}$ *cis*-1,2-cyclopentanediol + MnO_2+ OH^-

(c) Cyclopentanol + $HNO_3 \xrightarrow{\text{(hot)}} HO_2C(CH_2)_3CO_2H + NO_2 + H_2O$

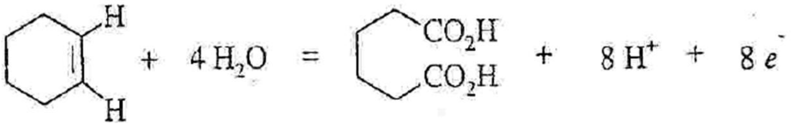
(d) 1,2,3-Cyclohexanetriol + $HIO_4 \xrightarrow{\text{(cold)}} OCH(CH_2)_3CHO + HCO_2H + HIO_3$

SOLUTIONS TO SAMPLE PROBLEMS

(a) Reduction:

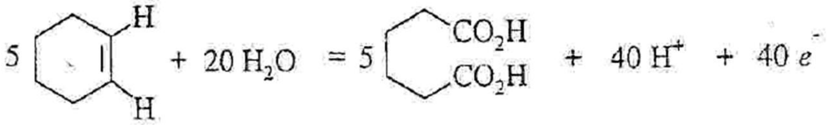
$$\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,e^- = \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O}$$

Oxidation:

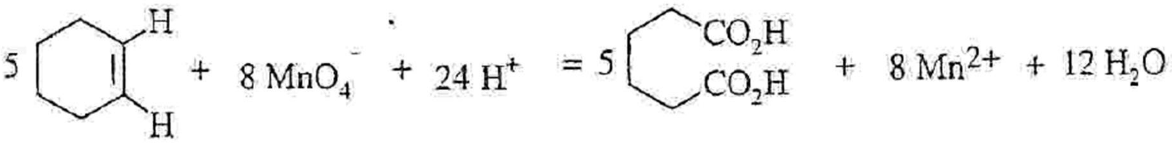


The least common multiple is 40:

$$8\,\mathrm{MnO_4^-} + 64\,\mathrm{H^+} + 40\,e^- = 8\,\mathrm{Mn^{2+}} + 32\,\mathrm{H_2O}$$



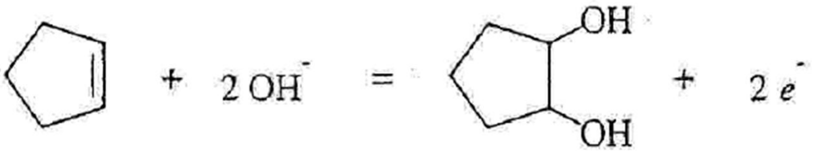
Adding and canceling:



(b) Reduction:

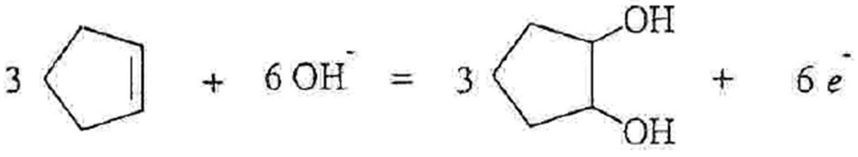
$$\mathrm{MnO_4^-} + 2\,\mathrm{H_2O} + 3\,e^- = \mathrm{MnO_2} + 4\,\mathrm{OH^-}$$

Oxidation:

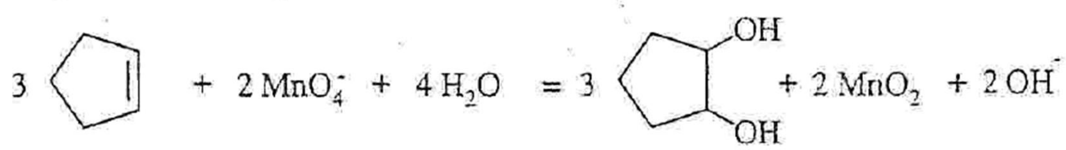


The least common multiple is 6:

$$2\,\mathrm{MnO_4^-} + 4\,\mathrm{H_2O} + 6\,e^- = 2\,\mathrm{MnO_2} + 8\,\mathrm{OH^-}$$



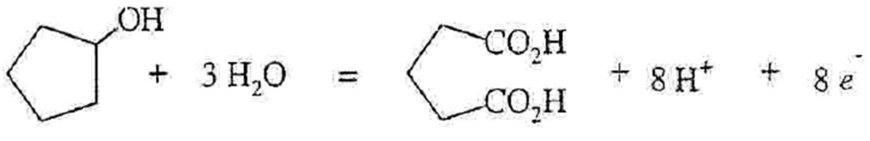
Adding and cancelling:



(c) Reduction:

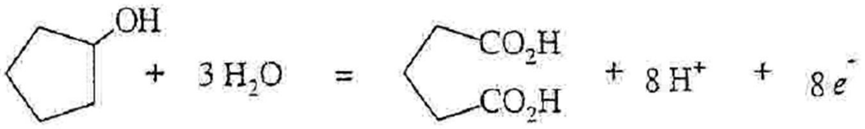
$$HNO_3 + H^+ + e^- = NO_2 + H_2O$$

Oxidation:

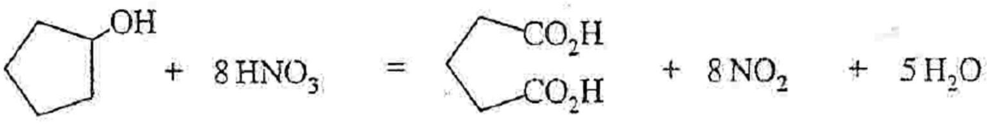


The least common multiple is 8:

$$8\,HNO_3 + 8\,H^+ + 8\,e^- = 8\,NO_2 + 8\,H_2O$$



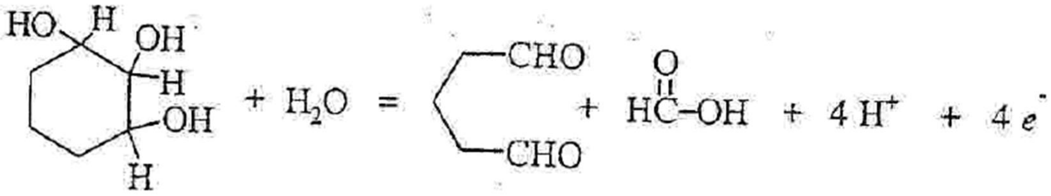
Adding and cancelling:



(d) Reduction:

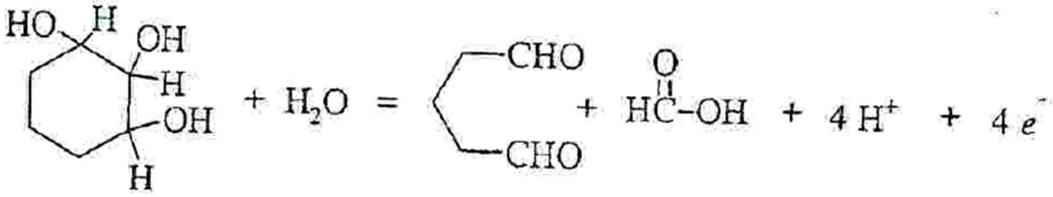
$$HIO_4 + 2\,H^+ + 2\,e^- = HIO_3 + H_2O$$

Oxidation:

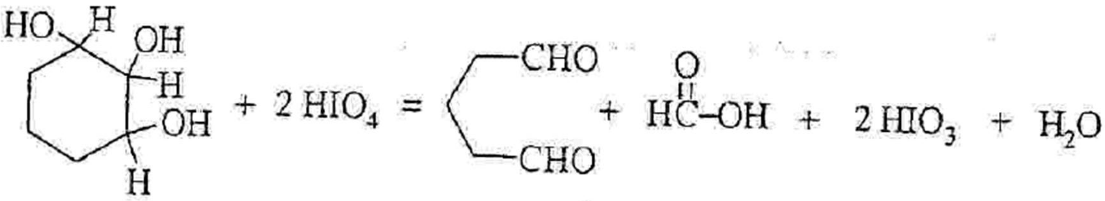


The least common multiple is 4:

$$2\,HIO_4 + 4\,H^+ + 4\,e^- = 2\,HIO_3 + 2\,H_2O$$

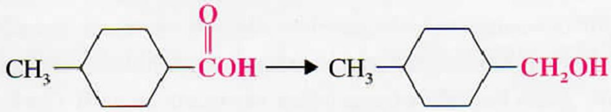


Adding and cancelling:

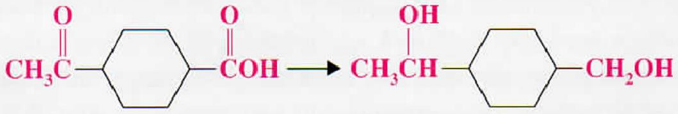


Aşağıdaki dönüşümleri gerçekleştirmek için hangi indirgeni, $LiAlH_4$ ya da $NaBH_4$, kullanırsınız? **Problem 12.4**

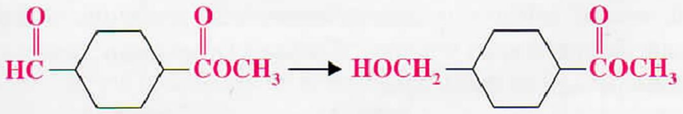
(a)



(b)



(c)



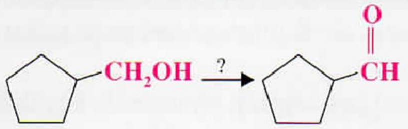
12.4 (a) $LiAlH_4$

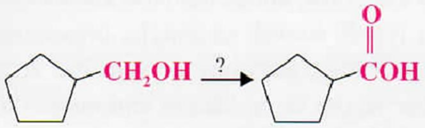
(b) $LiAlH_4$

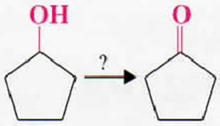
(c) $NaBH_4$

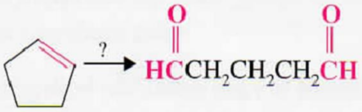
Problem 12.5

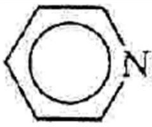
Aşağıdaki her bir dönüşümün nasıl gerçekleştirilebileceğini gösteriniz.

(a)


(b)


(c)


(d)


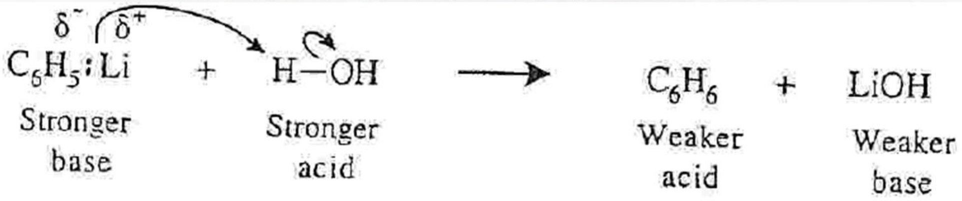
12.5 (a)

NH$^+$ CrO_3Cl^-(PCC)/CH_2Cl_2

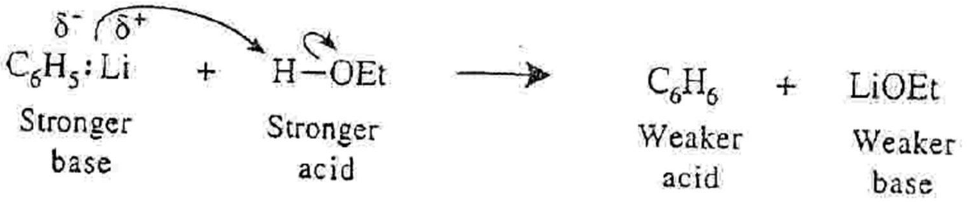
(b) $KMnO_4$, OH^-, H_2O, heat; then H_3O^+

(c) H_2CrO_4/acetone

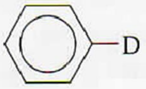
(d) (1) O_3 (2) Zn, HOAc

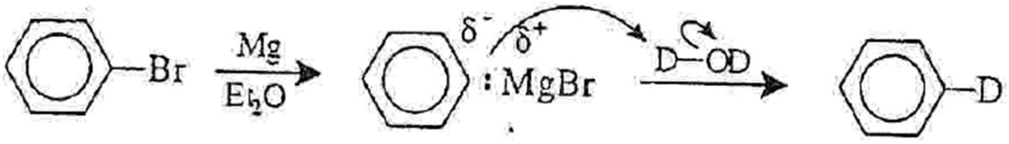
Problem 12.6 ➤ Fenillityum (a) su ve (b) etanolle etkileştirildiğinde meyadan gelecek tepkimeler için yukarıda verilenlere benzer eşitlikler yazınız. Dha kuvvetli ve daha zayıf asitleri, daha kuvvetli ve daha zayıf bazları gösteriniz.

12.6 (a)


(b)


Problem 12.7 ➤ Elinizin altında bromobenzen (C_6H_5Br), magnezyum, kuru eter ve döteryum oksit (D_2O) bulunduğunu varsayarak, aşağıdaki döteryumla etiketlenmiş bileşiği nasıl sentezleyebileceğinizi gösteriniz.

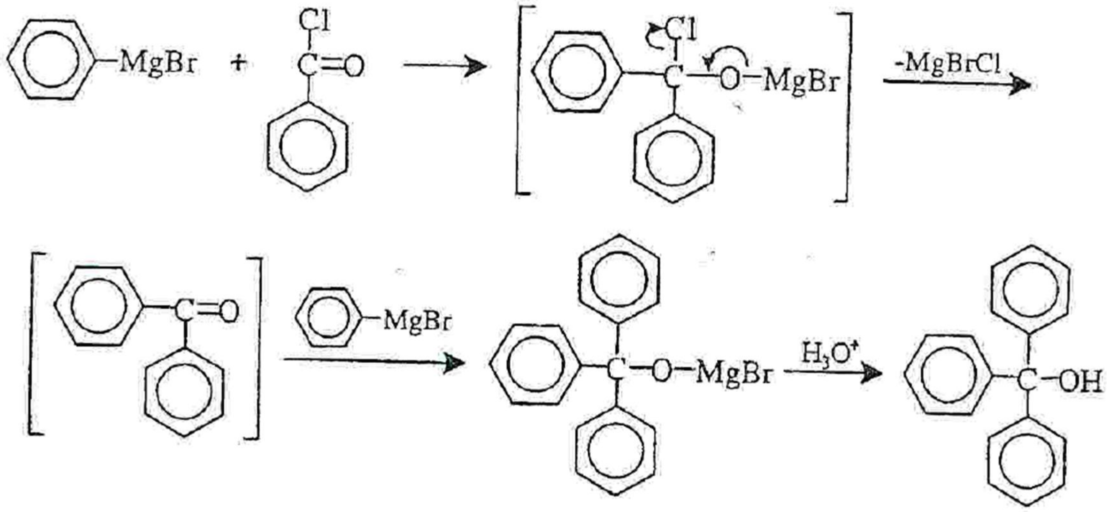


12.7


Problem 12.8 ➤

Fenilmagnezyum bromür, benzoil klorürle, $C_6H_5\overset{O}{\overset{\|}{C}}Cl$, tepkimeye girerek trifenilmetanolü, $(C_6H_5)_3COH$, oluşturur. Bu tepkime, Grignard reaktiflerinin açil klorürlerle verdiği tipik bir tepkimedir ve mekanizması bir Grignard reaktifinin bir esterle verdiği, biraz önce gösterilen tepkimenin mekanizmasına benzemektedir. Trifenilmetanolün oluşumunun basamaklarını gösteriniz.

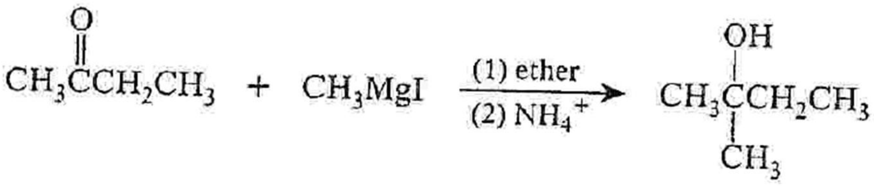
12.8



Aşağıdaki bileşiklerin sentezi için Grignard tepkimelerini nasıl kullanabileceğinizi gösteriniz. (Bir organik halojenürle başlamalısınız ve gerekli olan diğer bileşikleri kullanabilirsiniz.) ◄ **Problem 12.9**

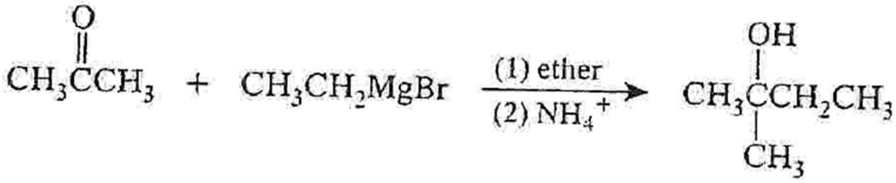
(a) 2-Metil-2-bütanol (üç yoldan)
(b) 3-Metil-3-pentanol (üç yoldan)
(c) 3-Etil-2-pentanol (iki yoldan)
(d) 2-Fenil-2-pentanol (üç yoldan)
(e) Trifenilmetanol (iki yoldan)

12.9 (a) (1)



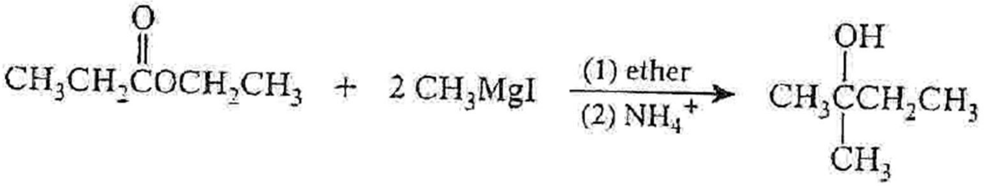
$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 + CH_3MgI \xrightarrow[(2)\ NH_4^+]{(1)\ ether} CH_3\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_3$$

(2)



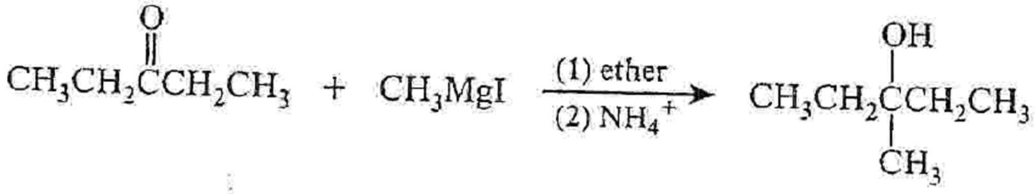
$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ ether} CH_3\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_3$$

(3)



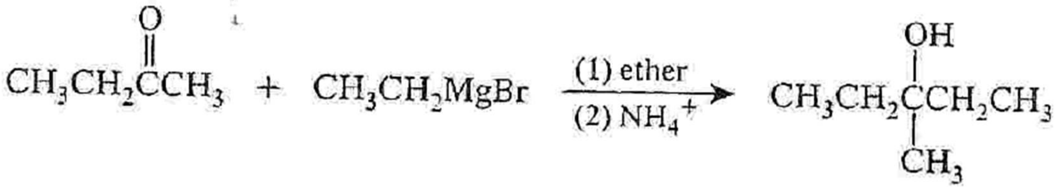
$$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 + 2\ CH_3MgI \xrightarrow[(2)\ NH_4^+]{(1)\ ether} CH_3\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_3$$

(b) (1)



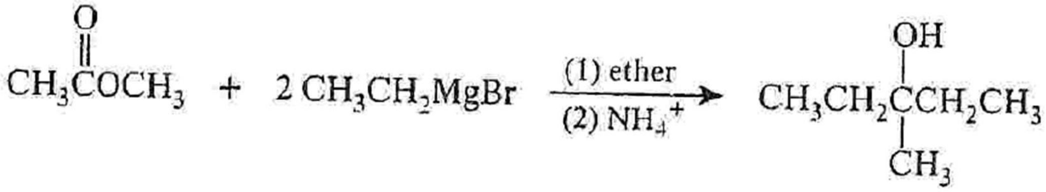
$$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 + CH_3MgI \xrightarrow[(2)\ NH_4^+]{(1)\ ether} CH_3CH_2\underset{CH_3}{\overset{OH}{C}}CH_2CH_3$$

(2)



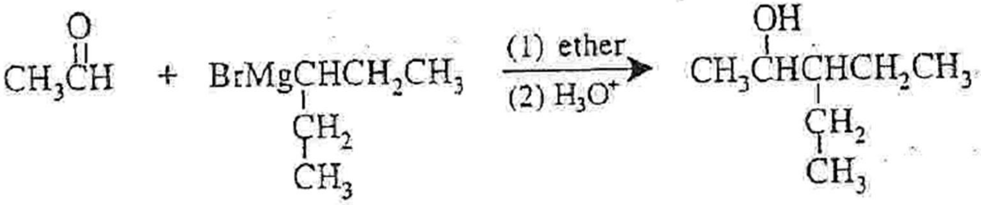
$$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 + CH_3CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ ether} CH_3CH_2\underset{CH_3}{\overset{OH}{C}}CH_2CH_3$$

(3)



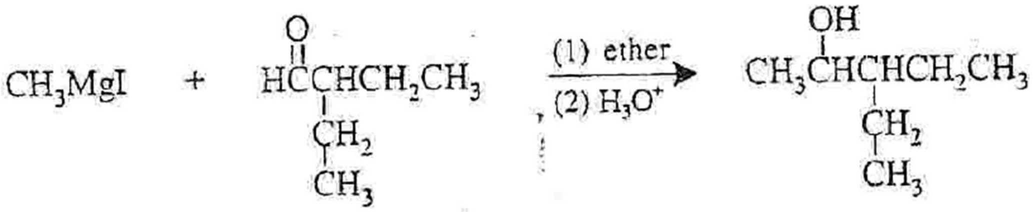
$$CH_3\overset{\overset{O}{\|}}{C}OCH_3 + 2\ CH_3CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ ether} CH_3CH_2\underset{CH_3}{\overset{OH}{C}}CH_2CH_3$$

(c) (1)



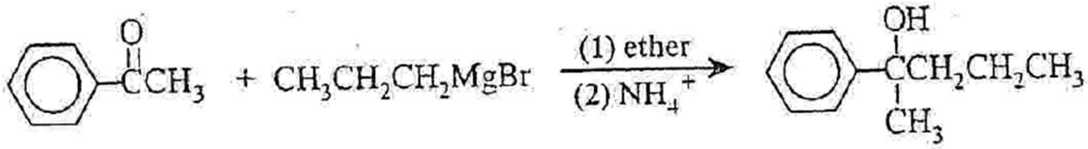
$$CH_3\overset{\overset{O}{\|}}{C}H + BrMg\underset{\underset{CH_3}{CH_2}}{C}HCH_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ ether} CH_3\overset{OH}{C}H\underset{\underset{CH_3}{CH_2}}{C}HCH_2CH_3$$

(2)

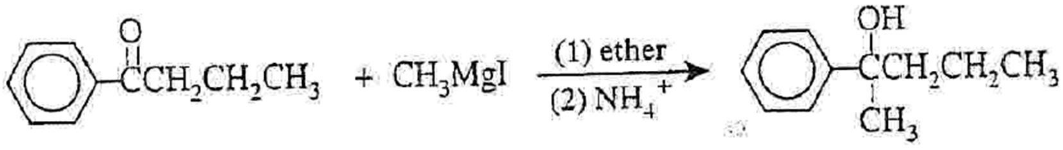


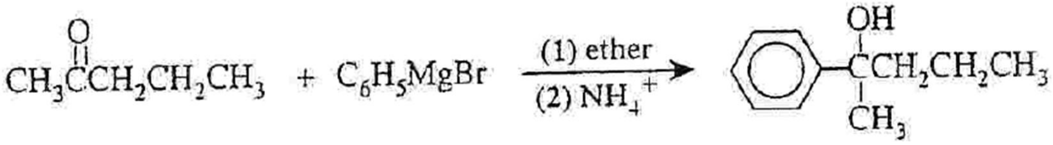
$$CH_3MgI + H\overset{\overset{O}{\|}}{C}\underset{\underset{CH_3}{CH_2}}{C}HCH_2CH_3 \xrightarrow[(2)\ H_3O^+]{(1)\ ether} CH_3\overset{OH}{C}H\underset{\underset{CH_3}{CH_2}}{C}HCH_2CH_3$$

(d) (1)

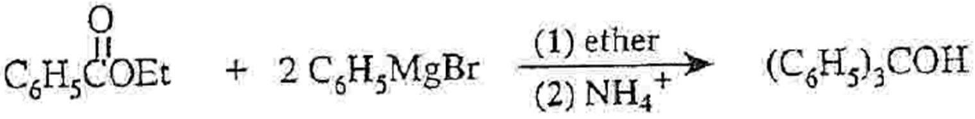


(2)



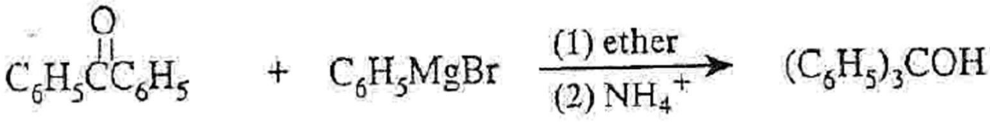


(e) (1)



$$C_6H_5\overset{\overset{O}{\|}}{C}OEt + 2\ C_6H_5MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ ether} (C_6H_5)_3COH$$

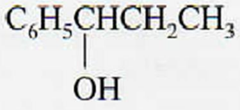
(2)

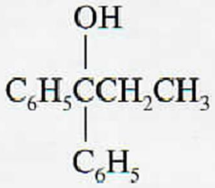


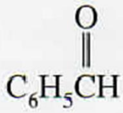
$$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5 + C_6H_5MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ ether} (C_6H_5)_3COH$$

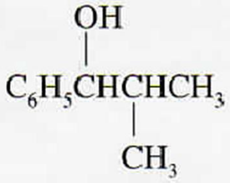
Problem 12.10

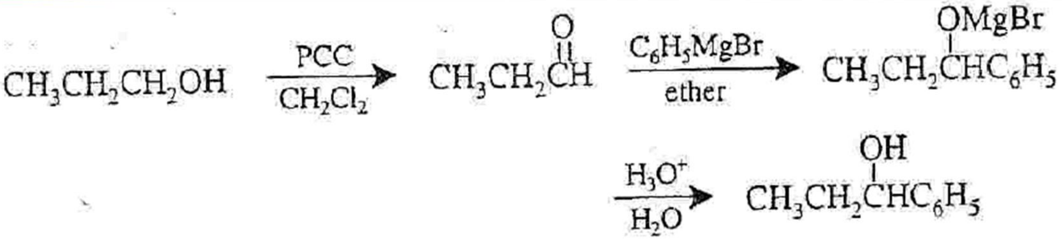
Aşağıdakilerin her birinin sentezini tasarlayınız. Başlangıç maddesi olarak fenilmagnezyum bromür, oksiran, formaldehit, dört ya da daha az sayıda karbon atomu içeren alkolleri veya esterleri kullanmanıza izin verilmektedir. İnorganik reaktifleri ve piridinyum klorokromat (PCC) gibi yükseltgenleri kullanabilirsiniz.

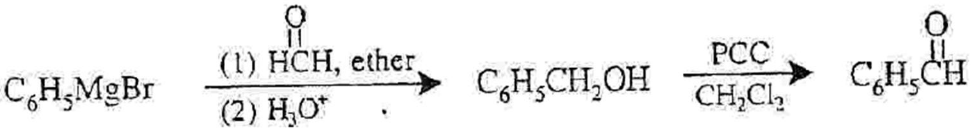
(a) 
$C_6H_5\underset{OH}{CH}CH_2CH_3$

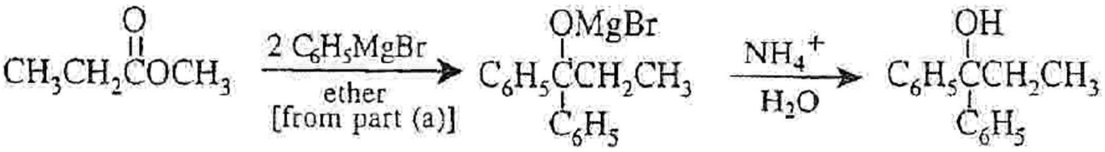
(c) 
$C_6H_5\overset{OH}{\underset{C_6H_5}{C}}CH_2CH_3$

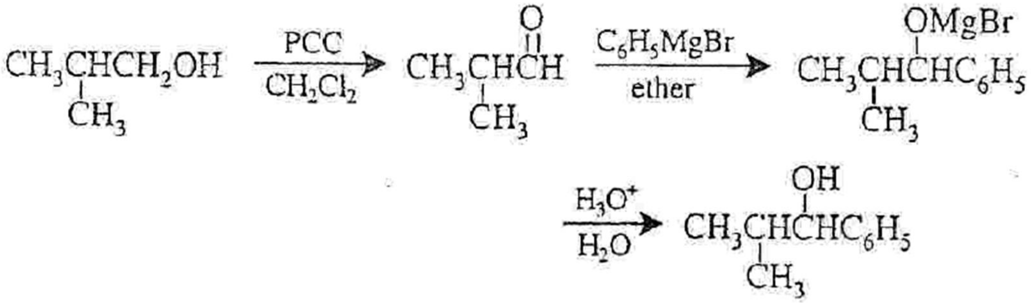
(b) 
$C_6H_5\overset{O}{\overset{\|}{C}}H$

(d) 
$C_6H_5\overset{OH}{CH}\underset{CH_3}{CH}CH_3$

12.10 (a) 
$CH_3CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2\overset{O}{\overset{\|}{C}}H \xrightarrow[ether]{C_6H_5MgBr} CH_3CH_2\overset{OMgBr}{C}HC_6H_5 \xrightarrow[H_2O]{H_3O^+} CH_3CH_2\overset{OH}{C}HC_6H_5$

(b) 
$C_6H_5MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ H\overset{O}{\overset{\|}{C}}H,\ ether} C_6H_5CH_2OH \xrightarrow[CH_2Cl_2]{PCC} C_6H_5\overset{O}{\overset{\|}{C}}H$

(c) 
$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[\text{ether [from part (a)]}]{2\ C_6H_5MgBr} C_6H_5\overset{OMgBr}{\underset{C_6H_5}{C}}CH_2CH_3 \xrightarrow[H_2O]{NH_4^+} C_6H_5\overset{OH}{\underset{C_6H_5}{C}}CH_2CH_3$

(d) 
$CH_3\underset{CH_3}{CH}CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3\underset{CH_3}{CH}\overset{O}{\overset{\|}{C}}H \xrightarrow[ether]{C_6H_5MgBr} CH_3\underset{CH_3}{CH}\overset{OMgBr}{C}HC_6H_5 \xrightarrow[H_2O]{H_3O^+} CH_3\underset{CH_3}{CH}\overset{OH}{C}HC_6H_5$

EK PROBLE

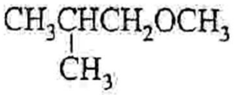
12.11 İzobütil bromürün, $(CH_3)_2CHCH_2Br$, aşağıdaki reaktiflerin herbiriyle tepkimesi sonunda hangi ürün (veya ürünler) oluşabilir?

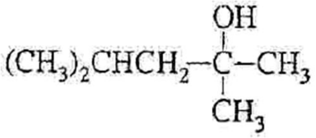
(a) OH^-, H_2O
(b) CN^-, etanol
(c) $(CH_3)_3CO^-$, $(CH_3)_3COH$
(d) CH_3O^-, CH_3OH
(e) Li, Et_2O, sonra $CH_3\overset{O}{\overset{\|}{C}}CH_3$, sonra NH_4Cl, H_2O
(f) Mg, Et_2O, sonra $CH_3\overset{O}{\overset{\|}{C}}H$, daha sonra H_3O^+
(g) Mg, Et_2O, sonra $CH_3\overset{O}{\overset{\|}{C}}OCH_3$, sonra NH_4Cl, H_2O
(h) Mg, Et_2O, sonra $H_2\overset{O}{C-C}H_2$, sonra H_3O^+
(i) Mg, Et_2O, sonra $H-\overset{O}{\overset{\|}{C}}-H$, sonra NH_4Cl, H_2O
(j) Li, Et_2O, sonra CH_3OH
(k) Li, Et_2O, sonra $CH_3C\equiv CH$

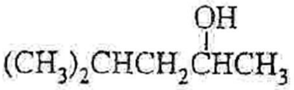
12.11 (a) $(CH_3)_2CHCH_2OH + (CH_3)_2C{=}CH_2$

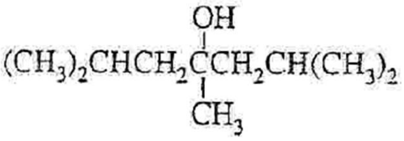
(b) $(CH_3)_2CHCH_2CN$

(c) $(CH_3)_2C{=}CH_2$

(d) 
$\underset{\displaystyle CH_3}{CH_3CHCH_2OCH_3}$ $+ (CH_3)_2C{=}CH_2$

(e) 
$(CH_3)_2CHCH_2{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}CH_3$

(f) 
$(CH_3)_2CHCH_2\overset{\displaystyle OH}{C}HCH_3$

(g) 
$(CH_3)_2CHCH_2\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}CH_2CH(CH_3)_2$

(h) $(CH_3)_2CHCH_2CH_2CH_2OH$

(i) $(CH_3)_2CHCH_2CH_2OH$

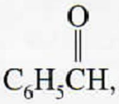
(j) $(CH_3)_2CHCH_3$

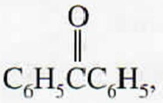
(k) $(CH_3)_2CHCH_3 \quad + \quad CH_3C{\equiv}CLi$

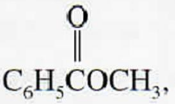
12.12 Etilmagnezyum bromürün (CH_3CH_2MgBr) aşağıdaki reaktiflerin her biriyle tepkimesinden hangi ürünlerin oluşmasını beklersiniz?

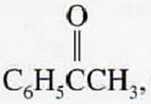
(a) H_2O

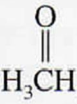
(b) D_2O

(c) 
$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}H$, sonra H_3O^+

(d) 
$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}C_6H_5$, sonra NH_4Cl, H_2O

(e) 
$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}OCH_3$, sonra NH_4Cl, H_2O

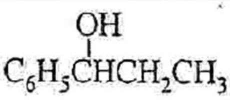
(f) 
$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}CH_3$, sonra NH_4Cl, H_2O

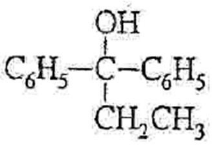
(g) $CH_3CH_2C{\equiv}CH$, sonra 
$CH_3\overset{\displaystyle O}{\overset{\|}{C}}H$, sonra H_3O^+

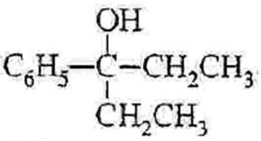
(h) Siklopentadien

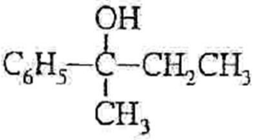
12.12 (a) CH_3CH_3

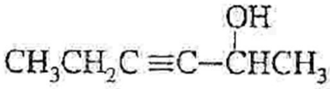
(b) CH_3CH_2D

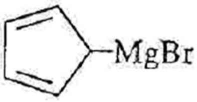
(c) 
$C_6H_5\overset{\displaystyle OH}{C}HCH_2CH_3$

(d) 
$C_6H_5{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_2CH_3}{C}}{-}C_6H_5$

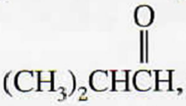
(e) 
$C_6H_5{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_2CH_3}{C}}{-}CH_2CH_3$

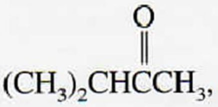
(f) 
$C_6H_5{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}{-}CH_2CH_3$

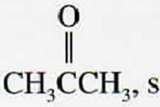
(g) $CH_3CH_3 \quad + \quad$ 
$CH_3CH_2C{\equiv}C{-}\overset{\displaystyle OH}{C}HCH_3$

(h) $CH_3CH_3 \quad +$ 

12.13 Propillityumun ($CH_3CH_2CH_2Li$), aşağıdaki reaktiflerin her biriyle tepkimesinden hangi ürünler meydana gelir?

(a)  $(CH_3)_2CH\overset{O}{\overset{\|}{C}}H$, sonra H_3O^+

(b)  $(CH_3)_2CH\overset{O}{\overset{\|}{C}}CH_3$, sonra NH_4Cl, H_2O

(c) 1-Pentin, sonra  $CH_3\overset{O}{\overset{\|}{C}}CH_3$, sonra NH_4Cl, H_2O

(d) Etanol

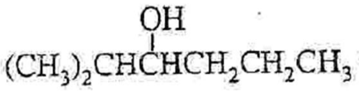
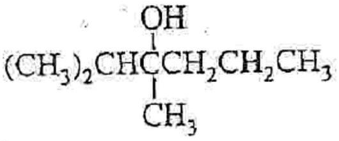
(e) CuI, sonra $CH_2{=}CHCH_2Br$

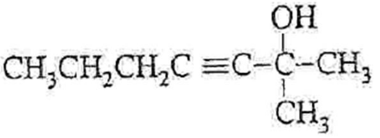
(f) CuI, sonra siklopentil bromür

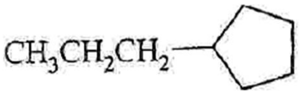
(g) CuI, sonra (*Z*)-1-iyodopropan

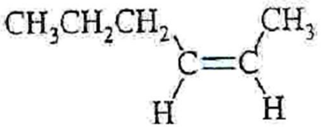
(h) CuI, sonra CH_3I

(i) CH_3CO_2D

12.13 (a)  $(CH_3)_2CH\overset{OH}{\overset{|}{C}}HCH_2CH_2CH_3$ (b)  $(CH_3)_2CH\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_2CH_3$

(c) $CH_3CH_2CH_3$ +  $CH_3CH_2CH_2C\equiv C-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$ (d) $CH_3CH_2CH_3$

(e) $CH_3CH_2CH_2CH_2CH{=}CH_2$ (f) 

(g)  (h) $CH_3CH_2CH_2CH_3$

Note: This variation of the Corey-Posner, Whitesides-House synthesis is stereospecific.

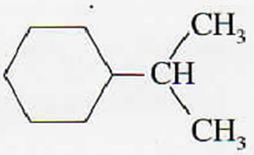
(i) $CH_3CH_2CH_2D$

12.14 Aşağıdaki dönüşümleri uygulamak için hangi yükseltgen ya da indirgenleri kullanırsınız?

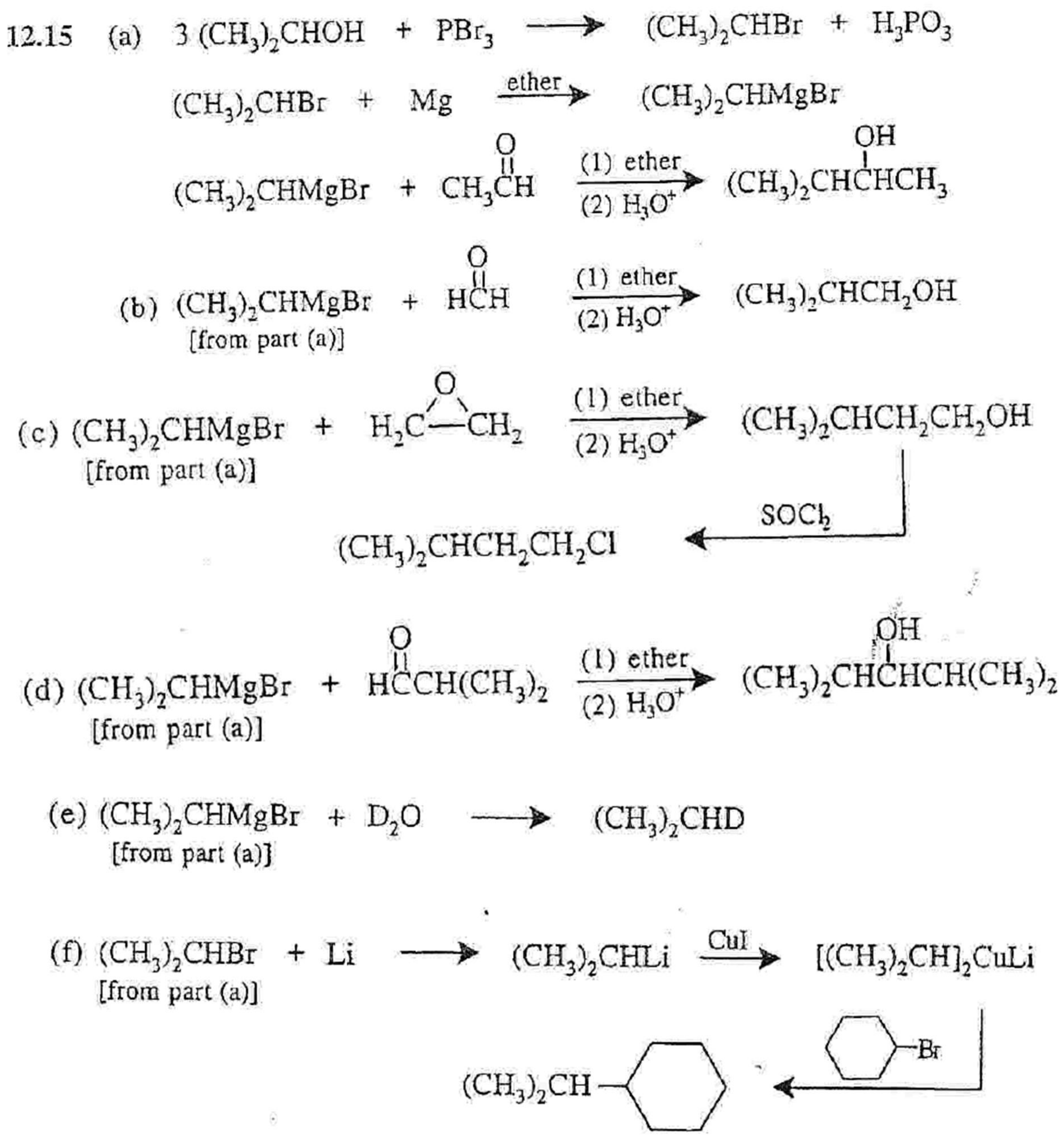
(a) $CH_3COCH_2CH_2CO_2CH_3 \longrightarrow CH_3CHOHCH_2CH_2CH_2OH + CH_3OH$
(b) $CH_3COCH_2CH_2CO_2CH_3 \longrightarrow CH_3CHOHCH_2CH_2CO_2CH_3$
(c) $HO_2CCH_2CH_2CH_2CO_2H \longrightarrow HOCH_2CH_2CH_2CH_2CH_2OH$
(d) $HOCH_2CH_2CH_2CH_2CH_2OH \longrightarrow HO_2CCH_2CH_2CH_2CO_2H$
(e) $HOCH_2CH_2CH_2CH_2CH_2OH \longrightarrow OHCCH_2CH_2CH_2CHO$

12.14 (a) $LiAlH_4$
(b) $NaBH_4$
(c) $LiAlH_4$
(d) (1) $KMnO_4$, OH^-, heat, (2) H_3O^+
(e) PCC/CH_2Cl_2

12.15 İzopropil alkolün, $CH_3CH(OH)CH_3$, aşağıdaki ürünlere dönüştürüldüğü her bir sentezin tüm basamaklarını tasarlayınız.

(a) $(CH_3)_2CHCH(OH)CH_3$
(b) $(CH_3)_2CHCH_2OH$
(c) $(CH_3)_2CHCH_2CH_2Cl$
(d) $(CH_3)_2CHCH(OH)CH(CH_3)_2$
(e) CH_3CHDCH_3
(f) 

12.15



(a) $3\,(CH_3)_2CHOH + PBr_3 \longrightarrow (CH_3)_2CHBr + H_3PO_3$

$(CH_3)_2CHBr + Mg \xrightarrow{ether} (CH_3)_2CHMgBr$

$(CH_3)_2CHMgBr + CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow[(2)\ H_3O^+]{(1)\ ether} (CH_3)_2CH\overset{OH}{\overset{|}{C}}HCH_3$

(b) $(CH_3)_2CHMgBr + H\overset{O}{\overset{\|}{C}}H \xrightarrow[(2)\ H_3O^+]{(1)\ ether} (CH_3)_2CHCH_2OH$
[from part (a)]

(c) $(CH_3)_2CHMgBr + H_2C\overset{O}{—}CH_2 \xrightarrow[(2)\ H_3O^+]{(1)\ ether} (CH_3)_2CHCH_2CH_2OH \xrightarrow{SOCl_2} (CH_3)_2CHCH_2CH_2Cl$
[from part (a)]

(d) $(CH_3)_2CHMgBr + H\overset{O}{\overset{\|}{C}}CH(CH_3)_2 \xrightarrow[(2)\ H_3O^+]{(1)\ ether} (CH_3)_2CH\overset{OH}{\overset{|}{C}}HCH(CH_3)_2$
[from part (a)]

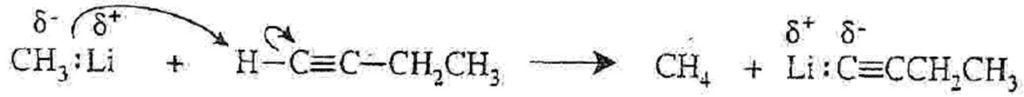
(e) $(CH_3)_2CHMgBr + D_2O \longrightarrow (CH_3)_2CHD$
[from part (a)]

(f) $(CH_3)_2CHBr + Li \longrightarrow (CH_3)_2CHLi \xrightarrow{CuI} [(CH_3)_2CH]_2CuLi$
[from part (a)]

12.16 Aşağıdaki tepkimelerin her birisinden hangi organik ürünler elde edilir?

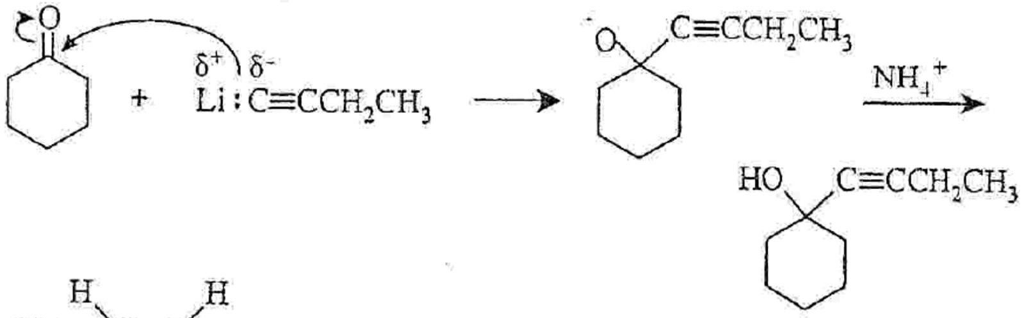
(a) Metillityum + 1-bütin $\longrightarrow$
(b) (a)'nın ürünü + siklohekzanon, sonra NH_4Cl, H_2O $\longrightarrow$
(c) (b)'nin ürünü + Ni_2B (P-2) ve H_2 $\longrightarrow$
(d) (b)'nin ürünü + NaH, sonra $CH_3CH_2OSO_2CH_3$ $\longrightarrow$
(e) $CH_3CH_2COCH_3$ + $NaBH_4$ $\longrightarrow$
(f) (e)'nin ürünü + mesil klorür $\xrightarrow{baz}$
(g) (f)'nin ürünü + CH_3CO_2Na $\longrightarrow$
(h) (g)'nin ürünü + $LiAlH_4$, sonra H_2O $\longrightarrow$

12.16 (a)

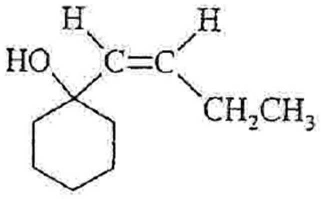


$$\overset{\delta^-}{CH_3}:\overset{\delta^+}{Li} + H-C\equiv C-CH_2CH_3 \longrightarrow CH_4 + \overset{\delta^+}{Li}:\overset{\delta^-}{C}\equiv CCH_2CH_3$$

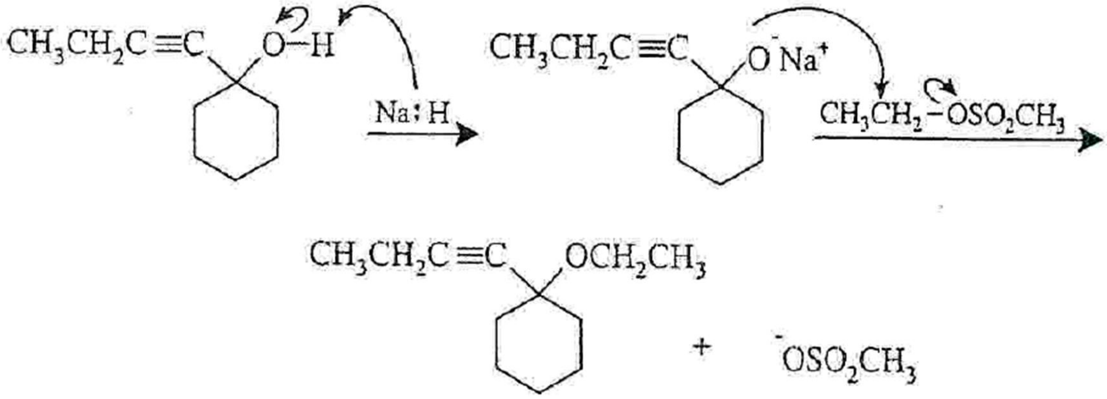
(b)



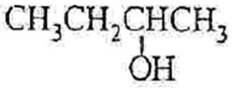
(c)



(d)

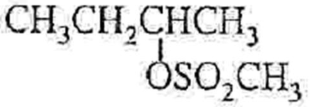


(e)



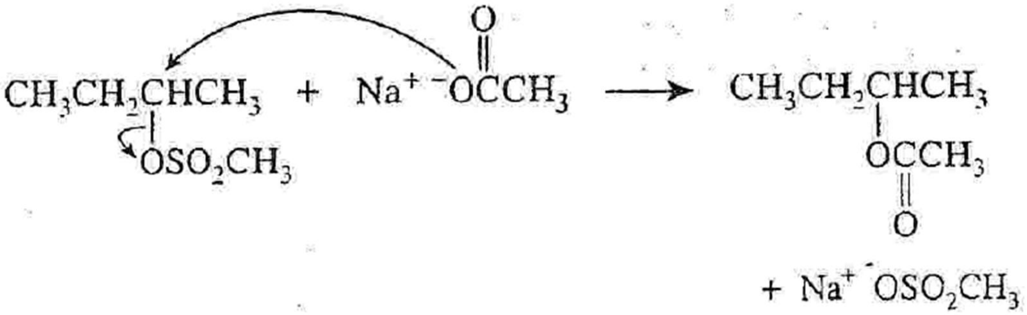
$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

(f)



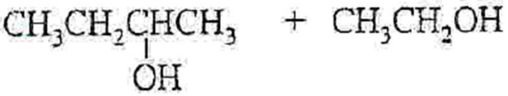
$$CH_3CH_2\underset{\displaystyle OSO_2CH_3}{\underset{|}{C}}HCH_3$$

(g)



$$CH_3CH_2\underset{\displaystyle OSO_2CH_3}{\underset{|}{C}}HCH_3 + Na^+\ ^-O\overset{\displaystyle O}{\overset{\|}{C}}CH_3 \longrightarrow CH_3CH_2\underset{\displaystyle O\underset{\displaystyle O}{\underset{\|}{C}}CH_3}{\underset{|}{C}}HCH_3 + Na^+\ ^-OSO_2CH_3$$

(h)



$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 + CH_3CH_2OH$$

12.17 1-Pentanolün, aşağıda verilen bileşiklere nasıl dönüştürülebileceğini gösteriniz. (Gerekli inorganik reaktifleri kullanabilirsiniz ve bir bileşiğin sentezini birden fazla göstermeniz gerekmez.)

(a) 1-Bromopentan	**(i)** 2-Pentanon ($CH_3COCH_2CH_2CH_3$)
(b) 2-Penten	**(j)** Pentanoik asit ($CH_3CH_2CH_2CH_2CO_2H$)
(c) 2-Pentanol	**(k)** Dipentil eter (iki yol)
(d) Pentan	**(l)** 1-Pentin
(e) 2-Bromopentan	**(m)** 2-Bromo-1-penten
(f) 1-Heksanol	**(n)** Pentillityum
(g) 1-Heptanol	**(o)** Dekan
(h) Pentanal ($CH_3CH_2CH_2CH_2CHO$)	**(p)** 4-Metil-4-nonanol

12.17 (a) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CH_2CH_2Br$

(b) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_3CH_2CH_2CH{=}CH_2$
[from (a)]

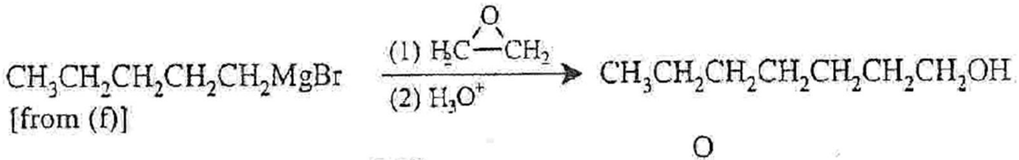
(c) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[(2)\ NaBH_4/OH^-]{(1)\ Hg(OAc)_2/THF\text{-}H_2O} CH_3CH_2CH_2\underset{OH}{C}HCH_3$
[from (b)]

(d) $CH_3CH_2CH_2\underset{OH}{C}HCH_3 \xrightarrow[\text{acetone, } H_2O]{H_2CrO_4} CH_3CH_2CH_2\underset{O}{\overset{\|}{C}}CH_3$
[from (c)]

(e) $CH_3CH_2CH_2\underset{OH}{C}HCH_3 \xrightarrow{PBr_3} CH_3CH_2CH_2\underset{Br}{C}HCH_3$
[from (c)]

(f) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[Et_2O]{Mg} CH_3CH_2CH_2CH_2CH_2MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ H\overset{O}{\overset{\|}{C}}H}$
[from (a)]

$CH_3CH_2CH_2CH_2CH_2CH_2OH$

(g) 

$CH_3CH_2CH_2CH_2CH_2MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ H_2C\overset{O}{-}CH_2} CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$
[from (f)]

(h) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H$

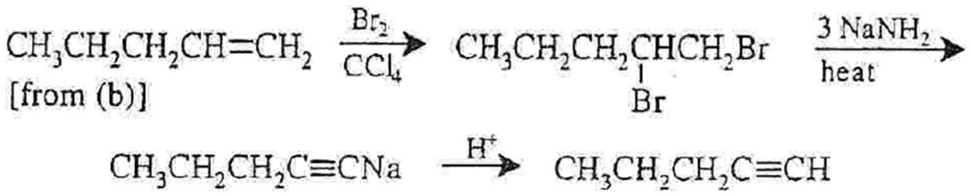
(i) $CH_3CH_2CH_2\underset{OH}{C}HCH_3 \xrightarrow[\text{acetone, } H_2O]{H_2CrO_4} CH_3CH_2CH_2\underset{O}{\overset{\|}{C}}CH_3$
[from (c)]

(j) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ \text{heat}} CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OH$

(k) (1) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[140°\ C]{H_2SO_4} (CH_3CH_2CH_2CH_2CH_2)_2O$

(2) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[(-H_2)]{NaH} CH_3CH_2CH_2CH_2CH_2ONa$

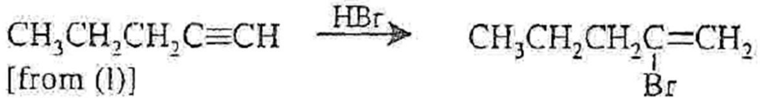
$\xrightarrow[\text{[from (a)]}]{CH_3CH_2CH_2CH_2CH_2Br} (CH_3CH_2CH_2CH_2CH_2)_2O$

(l) 

$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[heat]{3\,NaNH_2}$$

[from (b)]

$$CH_3CH_2CH_2C{\equiv}CNa \xrightarrow{H^+} CH_3CH_2CH_2C{\equiv}CH$$

(m) 

$$CH_3CH_2CH_2C{\equiv}CH \xrightarrow{HBr} CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}{=}CH_2$$

[from (l)]

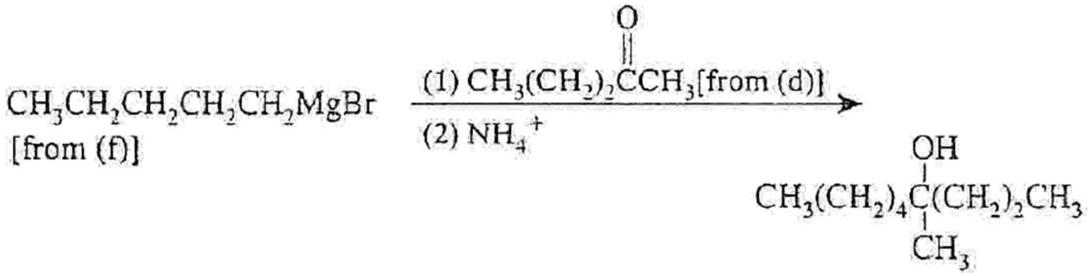
(n) $CH_3CH_2CH_2CH_2CH_2Br \xrightarrow[Et_2O]{Li} CH_3CH_2CH_2CH_2CH_2Li$

[from (a)]

(o) $CH_3CH_2CH_2CH_2CH_2Li \xrightarrow{CuI} (CH_3CH_2CH_2CH_2CH_2)_2CuLi$

[from (n)]

$$\xrightarrow[\text{[from (a)]}]{CH_3CH_2CH_2CH_2CH_2Br} CH_3(CH_2)_8CH_3$$

(p) 

$$CH_3CH_2CH_2CH_2CH_2MgBr \xrightarrow[(2)\ NH_4^+]{(1)\ CH_3(CH_2)_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3\text{[from (d)]}} CH_3(CH_2)_4\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}(CH_2)_2CH_3$$

[from (f)]

12.18 Aşağıdaki her bir dönüşümün nasıl gerçekleştirilebileceğini gösteriniz.

(a) Feniletilen ⟶ $C_6H_5C{\equiv}CC(OH)(CH_3)_2$

(b) $C_6H_5COCH_3$ ⟶ 1-feniletanol

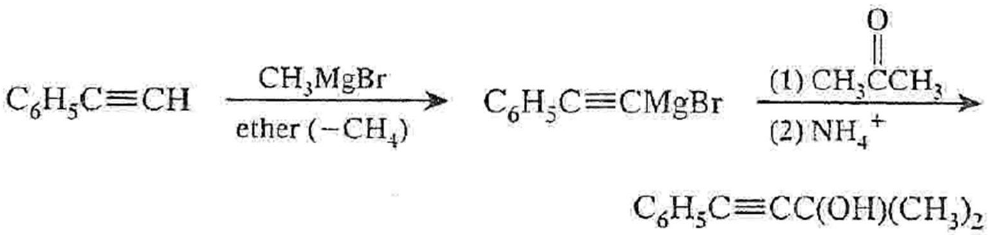
(c) **Feniletin ⟶ fenileten**

(d) **Fenileten ⟶ 2-feniletanol**

(e) **2-Feniletanol ⟶ 4-fenilbütanol**

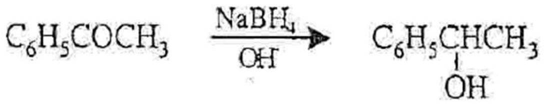
(f) **2-Fenilbütanol ⟶ 1-metoksi-2-feniletan**

12.18 (a)



$$C_6H_5C{\equiv}CH \xrightarrow[\text{ether }(-CH_4)]{CH_3MgBr} C_6H_5C{\equiv}CMgBr \xrightarrow[(2)\ NH_4^{\ +}]{(1)\ CH_3\overset{\overset{O}{\|}}{C}CH_3} C_6H_5C{\equiv}CC(OH)(CH_3)_2$$

(b)

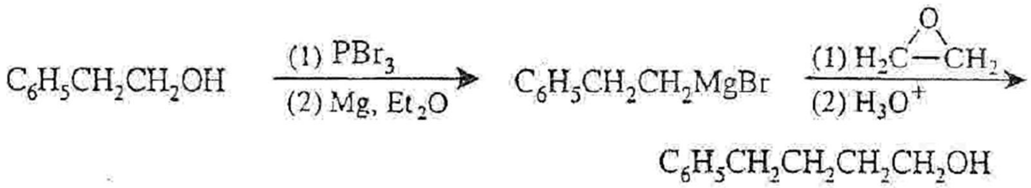


$$C_6H_5COCH_3 \xrightarrow[OH]{NaBH_4} C_6H_5\underset{\underset{OH}{|}}{C}HCH_3$$

(c) $C_6H_5C{\equiv}CH \xrightarrow[Ni_2B\ (P\text{-}2)]{H_2} C_6H_5CH{=}CH_2$

(d) $C_6H_5CH{=}CH_2 \xrightarrow[(2)\ H_2O_2,\ OH]{(1)\ THF{:}\ BH_3} C_6H_5CH_2CH_2OH$

(e)



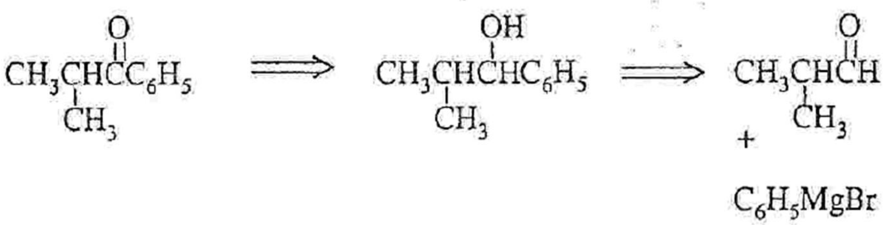
$$C_6H_5CH_2CH_2OH \xrightarrow[(2)\ Mg,\ Et_2O]{(1)\ PBr_3} C_6H_5CH_2CH_2MgBr \xrightarrow[(2)\ H_3O^+]{(1)\ H_2C\overset{O}{\text{—}}CH_2} C_6H_5CH_2CH_2CH_2CH_2OH$$

(f) $C_6H_5CH_2CH_2OH \xrightarrow[(-H_2)]{NaH} C_6H_5CH_2CH_2ONa \xrightarrow{CH_3I} C_6H_5CH_2CH_2OCH_3$

12.19 Kullanabileceğiniz dört karbon atomundan daha fazla karbon atomu içermeyen alkollere veya esterlere sahip olduğunuzu varsayarak, aşağıda verilen her bir bileşiği nasıl sentezleyebileceğinizi gösteriniz. Sentezin bir basamağında bir Grignard reaktifi kullanmalısınız. Eğer gerekirse oksiran ve bromobenzen kullanabilirsiniz; fakat gerekli olan diğer organik bileşiklerin nasıl sentezleneceğini göstermelisiniz. Gerekli olan çözücülere, yükseltgen ve indirgenler de dahil tüm inorganik reaktiflere sahip olduğunuzu varsayınız.

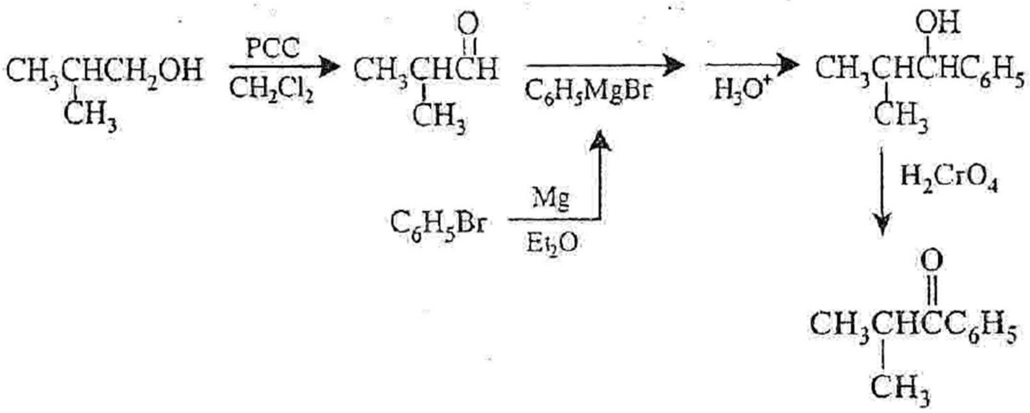
(a) $(CH_3)_2CHCOC_6H_5$
(b) 4-Etil-4-heptanol
(c) 1-Siklobütil-2-metil-1-propanol
(d) $C_6H_5CH_2CHO$
(e) $(CH_3)_2CHCH_2CH_2CO_2H$
(f) 1-Propilsiklobütanol
(g) $CH_3CH_2CH_2COCH_2CH(CH_3)_2$
(h) 3-Bromo-3-fenilpentan

12.19 (a) *Partial Analysis*



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}C_6H_5 \Longrightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle OH}{\overset{|}{C}}HC_6H_5 \Longrightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}H + C_6H_5MgBr$$

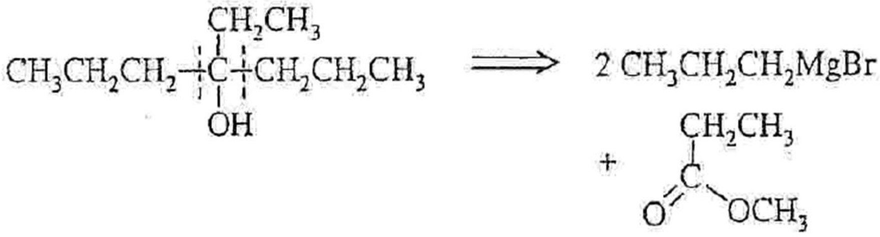
Synthesis



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}H \xrightarrow[C_6H_5MgBr]{} \xrightarrow[H_3O^+]{} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle OH}{\overset{|}{C}}HC_6H_5 \xrightarrow{H_2CrO_4} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}C_6H_5$$

$$C_6H_5Br \xrightarrow[Et_2O]{Mg} C_6H_5MgBr$$

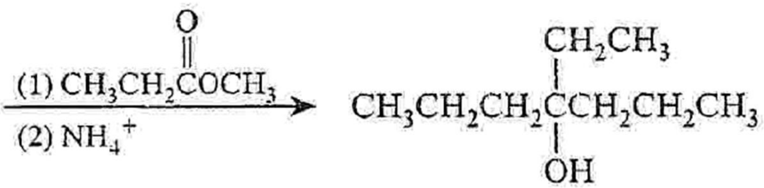
(b) *Partial Analysis*



$$CH_3CH_2CH_2\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle OH}{C}}CH_2CH_2CH_3 \Longrightarrow 2\ CH_3CH_2CH_2MgBr + O{=}\overset{\displaystyle CH_2CH_3}{C}{-}OCH_3$$

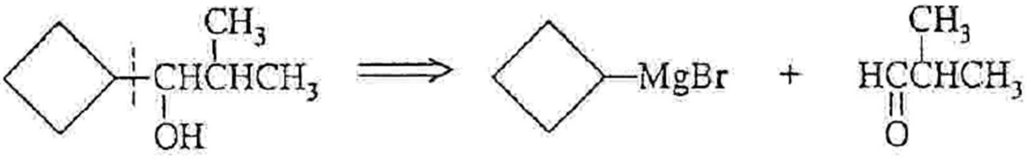
Synthesis

$CH_3CH_2CH_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2Br \xrightarrow[Et_2O]{Mg} CH_3CH_2CH_2MgBr$

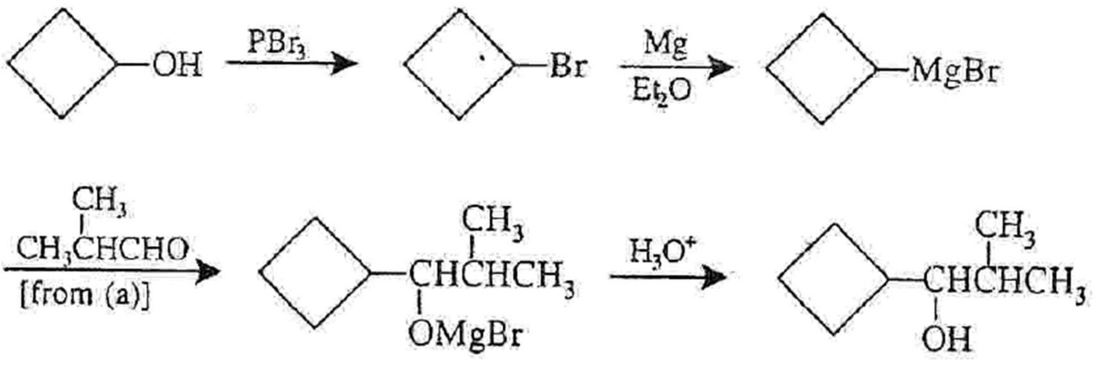


$$\xrightarrow[(2)\ NH_4^+]{(1)\ CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}OCH_3} CH_3CH_2CH_2\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle OH}{C}}CH_2CH_2CH_3$$

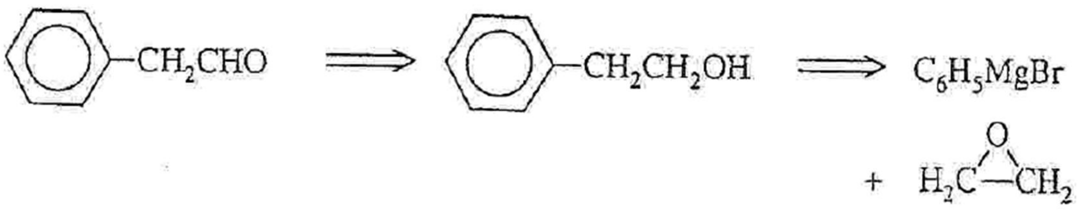
(c) *Partial Analysis*



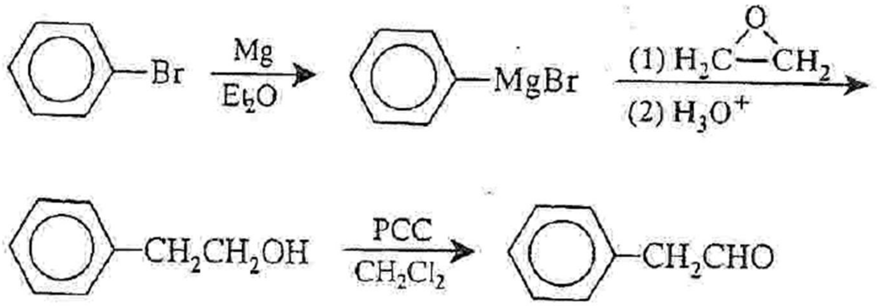
Synthesis



(d) *Partial Analysis*

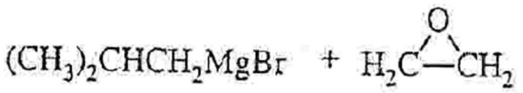


Synthesis



(e) *Partial Analysis*

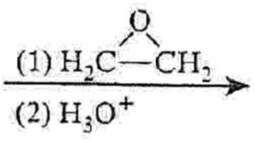
$(CH_3)_2CHCH_2CH_2CO_2H \Longrightarrow (CH_3)_2CHCH_2 \mid CH_2CH_2OH \Longrightarrow$



$(CH_3)_2CHCH_2MgBr + \overset{O}{H_2C-CH_2}$

Synthesis

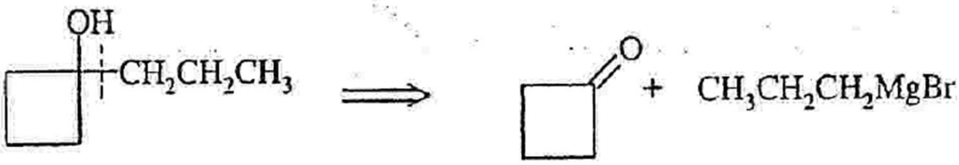
$(CH_3)_2CHCH_2OH \xrightarrow{PBr_3} (CH_3)_2CHCH_2Br \xrightarrow[Et_2O]{Mg} (CH_3)_2CHCH_2MgBr$



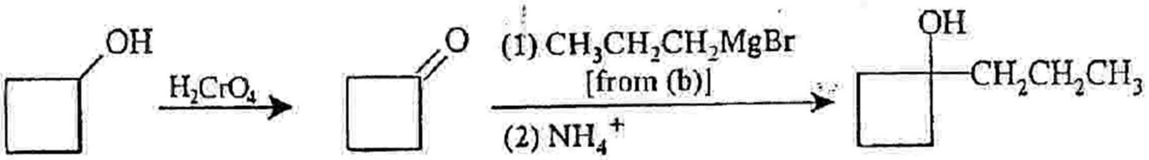
$\xrightarrow[(2)\ H_3O^+]{(1)\ \overset{O}{H_2C-CH_2}} (CH_3)_2CHCH_2CH_2CH_2OH \xrightarrow[(2)\ H_3O^+]{(1)\ KMnO_4,\ OH^-,\ heat}$

$(CH_3)_2CHCH_2CH_2CO_2H$

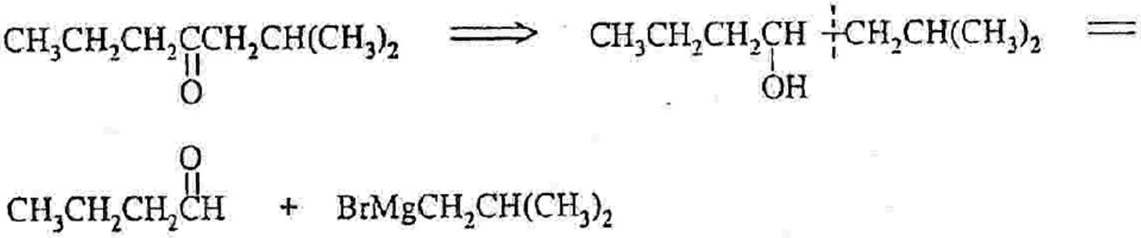
(f) *Partial Analysis*



Synthesis



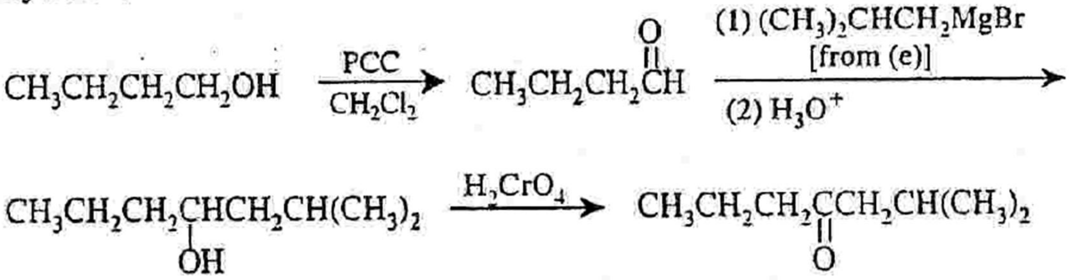
(g) *Partial Analysis*



$$CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH(CH_3)_2 \Longrightarrow CH_3CH_2CH_2\underset{\underset{OH}{|}}{CH} \vdots CH_2CH(CH_3)_2 \Longrightarrow$$

$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H + BrMgCH_2CH(CH_3)_2$$

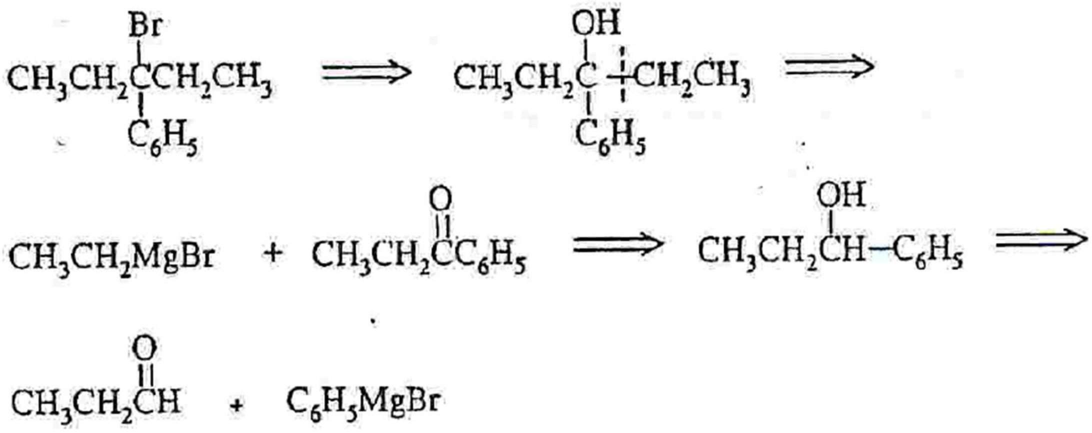
Synthesis



$$CH_3CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[(2)\ H_3O^+]{(1)\ (CH_3)_2CHCH_2MgBr\ [from\ (e)]}$$

$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_2CH(CH_3)_2 \xrightarrow{H_2CrO_4} CH_3CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH(CH_3)_2$$

(h) *Partial Analysis*

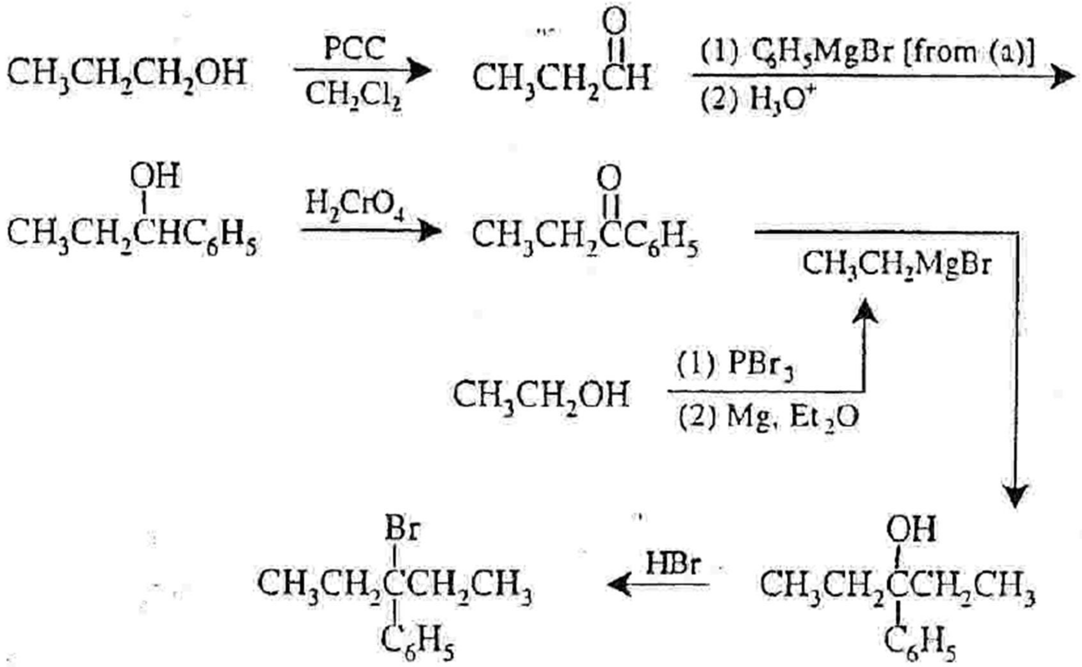


$$CH_3CH_2\overset{\overset{Br}{|}}{\underset{\underset{C_6H_5}{|}}{C}}CH_2CH_3 \Longrightarrow CH_3CH_2\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}} \vdots CH_2CH_3 \Longrightarrow$$

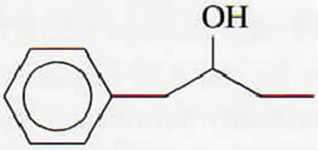
$$CH_3CH_2MgBr + CH_3CH_2\overset{\overset{O}{\|}}{C}C_6H_5 \Longrightarrow CH_3CH_2\overset{\overset{OH}{|}}{C}H{-}C_6H_5 \Longrightarrow$$

$$CH_3CH_2\overset{\overset{O}{\|}}{C}H + C_6H_5MgBr$$

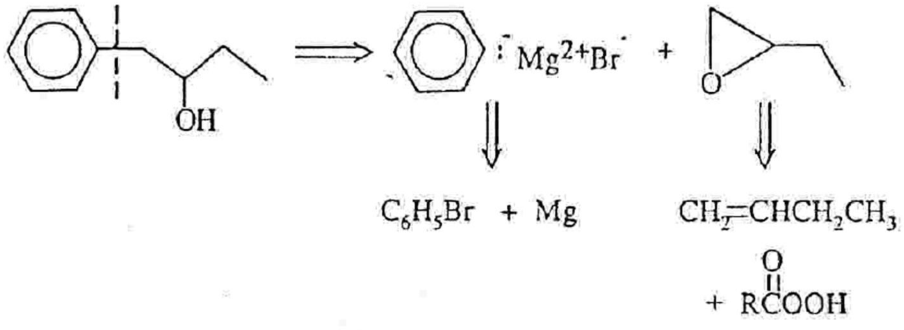
Synthesis



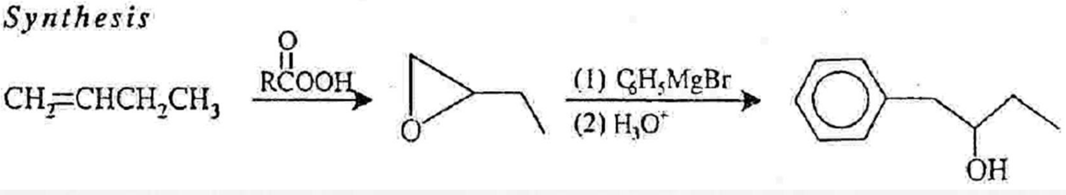
12.20 Aşağıda formülü verilen alkol, parfüm yapımında kullanılır. Bu alkolün, bromobenzen ve 1-bütenden sentezini gösteriniz.



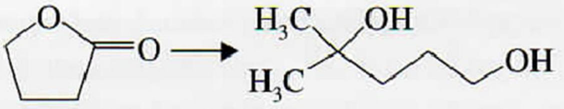
12.20 *Analysis*



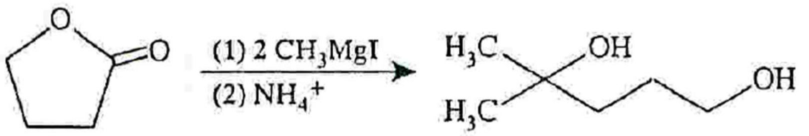
Synthesis



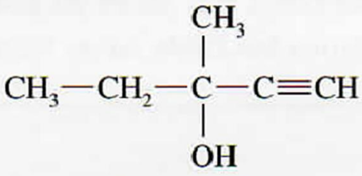
12.21 Aşağıdaki sentezde bir Grignard reaktifinin nasıl kullanılacağını gösteriniz.



12.21 The starting compound is a cyclic ester. Addition of two molar equivalents of CH_3MgI will (after acidification) furnish the desired product.



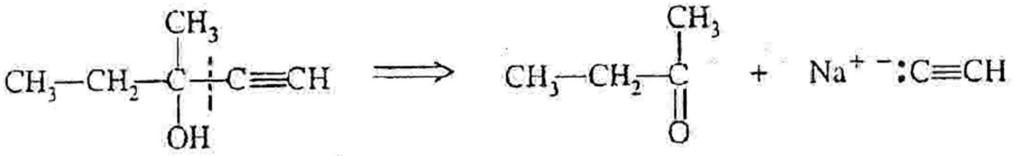
12.22 Dört veya daha az sayıda karbon atomu içeren bileşiklerle başlayarak, ılımlı bir hipnotik (uyku veren bileşik) olan rasemik meparfinolün sentezini tasarlayınız.



$$CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-C\equiv CH$$

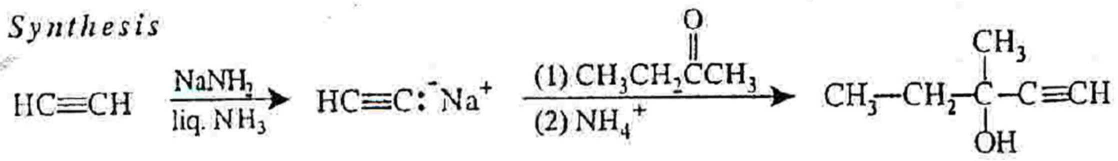
Meparfinol

12.22 *Analysis*



$$CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\,\vdots\,C\equiv CH \Longrightarrow CH_3-CH_2-\underset{\displaystyle O}{\overset{\displaystyle CH_3}{\overset{|}{\underset{\|}{C}}}} + Na^+\ {}^-{:}C\equiv CH$$

Synthesis



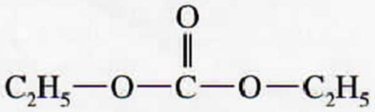
$$HC\equiv CH \xrightarrow[\text{liq. } NH_3]{NaNH_2} HC\equiv C{:}^-Na^+ \xrightarrow[(2)\ NH_4^+]{(1)\ CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3} CH_3-CH_2-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-C\equiv CH$$

12.23 Oksiran (oksasiklopropan) ve oksetan (oksasiklobütan), Grignard reaktifleri ve organolityum bileşikleriyle tepkimeye girerek alkolleri oluşturdukları halde, tetrahidrofuran (oksasiklopentan) o kadar istemsizdir ki bu bileşik organometalik bileşiklerin elde edilişinde çözücü olarak kullanılabilir. Bu oksijen içeren heterohalkalı bileşiklerin etkinlik farklarını açıklayınız.

12.23 The three- and four-membered rings are strained, and so they open on reaction with RMgX or RLi. THF possesses an essentially unstrained ring and hence is far more resistant to attack by an organometallic compound.

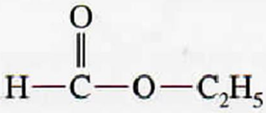
12.24 Bir Grignard reaktifinin aşağıdaki bileşiklerle tepkimesi sonunda oluşacak ürünleri tahmin ediniz.

(a) Dietil karbonat,



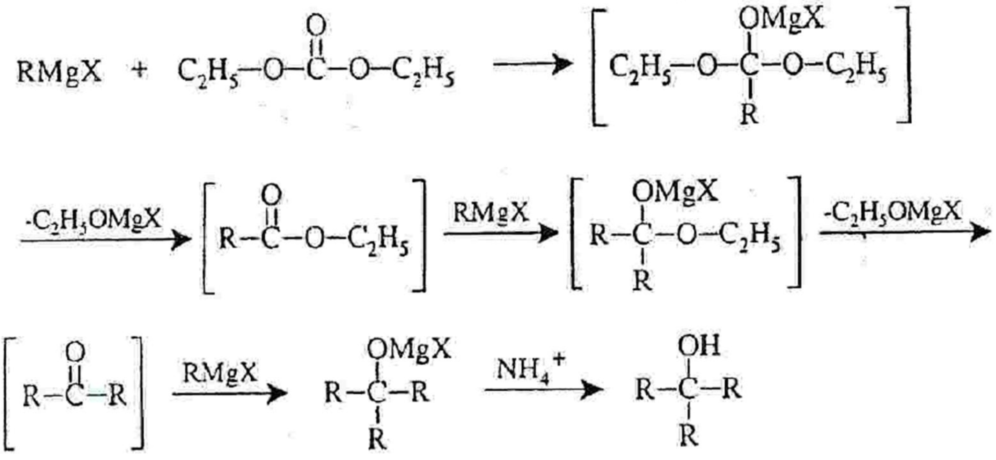
$$C_2H_5-O-\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5$$

(b) Etil format,

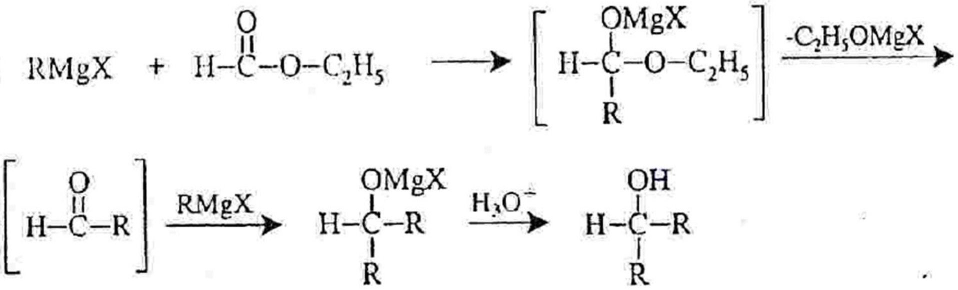


$$H-\overset{\displaystyle O}{\overset{\|}{C}}-O-C_2H_5$$

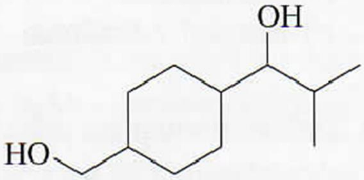
12.24 (a)



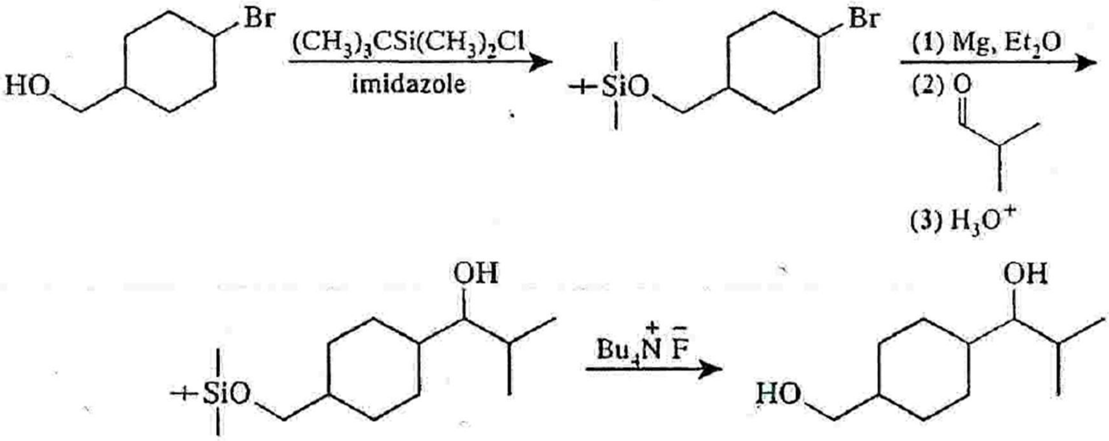
(b)



***12.25** Aşağıdaki bileşiği 1-bromo-4-hidroksimetilsikloheksan ve gerekli diğer reaktiflerden elde etmek için bir Grignard sentezi tasarlayınız.



***12.25**



Before converting the reactant to a Grignard reagent it is first necessary to mask the alcohol, such as by converting it to a *tert*-butyldimethylsilyl ether. After the Grignard reaction is over the protecting group is removed.

***12.26** 2-Feniletanol, 1,2-difeniletanol, 1,1-difeniletanol, 2,2-difeniletanoik asit ($(C_6H_5)_2CHCO_2H$) ve benzil 2-feniletanoatı ($C_6H_5CH_2CO_2CH_2C_6H_5$) birbirlerinden ayırdetmek için ^1H NMR, ^{13}C NMR, ve İR spektroskopisinden nasıl yararlanabileceğinizi açıklayınız.

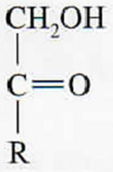
***12.26** 2-Phenylethanol, 1,2-diphenylethanol, and 1,1-diphenylethanol are distinct from diphenylacetic acid and benzyl phenylacetate in that they do not have carbonyl groups. IR spectroscopy can be used to segregate these compounds into two groups according to those that do or do not exhibit carbonyl absorptions.

^{1}H NMR can differentiate among all of the compounds. In the case of the alcohols, in the ^{1}H NMR spectrum of 2-phenylethanol there will be two triplets of equal integral value, whereas for 1,2-diphenylethanol there will be a doublet and a triplet in a 2:1 area ratio. The triplet will be downfield of the doublet. 1,1-Diphenylethanol will exhibit a singlet for the unsplit methyl hydrogens.

The broadband proton-decoupled ^{13}C NMR spectrum of 2-phenylethanol should show 6 signals (assuming no overlap), four of which are in the chemical shift region for aromatic carbons. 1,2-Diphenylethanol should exhibit 10 signals (assuming no overlap), 8 of which are in the aromatic region. 1,1-Diphenylethanol should show 6 signals (assuming no overlap), four of which would be in the aromatic region. The DEPT ^{13}C NMR spectra would give direct evidence as to the number of attached hydrogens on each carbon.

Regarding the carbonyl compounds, both diphenylacetic acid and benzyl phenylacetate will show carbonyl absorptions in the IR, but only the former will also have a hydroxyl absorption. The ^{1}H NMR spectrum of diphenylacetic acid should show a broad absorption for the carboxylic acid hydrogen and a sharp singlet for the unsplit hydrogen at C2. Their integral values should be the same, and approximately one tenth the integral value of the signals in the aromatic region. Benzyl phenylacetate will exhibit two singlets, one for each of the unsplit CH_2 groups. These signals will have an area ratio of 1:5 with respect to the signal for the 10 aromatic hydrogens. The broadband ^{1}H decoupled ^{13}C NMR spectrum for diphenylacetic acid should show four aromatic carbon signals, whereas that for benzyl phenylacetate (assuming no overlapping signals) would show 10 signals in the aromatic carbon region. Aside from the carbonyl and aromatic carbon signals, benzyl phenylacetate would show two additional signals, whereas diphenylacetic acid would show only one. DEPT ^{13}C NMR spectra for these two compounds would also distinguish them directly.

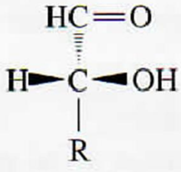
12.27 Sukroz (çay şekeri-sakkaroz) asit çözeltisiyle etkileştirildiğinde, bölünerek aşağıda görülen türden daha basit şekerleri oluşturur.



$$\begin{array}{c} CH_2OH \\ | \\ C{=}O \\ | \\ R \end{array}$$

A

ve



$$\begin{array}{c} HC{=}O \\ | \\ H-C-OH \\ | \\ R \end{array}$$

B

Daha sonra incelenecek nedenlerden dolayı, bu işlemlerin, sakkaroz gibi sakkaritlerle ilgili şekerlerin teşhisi için kullanılması durumunda analizden önce ürün karışımı çoğu kez sodyum borhidrürle etkileştirilir. Bu durum, başlangıç sakkaritlerin şeker yapı birimlerinin teşhisine ne gibi bir sınırlama getirir?

***12.27** It makes it impossible to distinguish between aldehyde and ketone type sugars (aldoses and ketoses) that had been components of the saccharide. Also, because the R groups of these sugars contain stereocenters, reduction of the ketone carbonyl will be stereoselective. This will complicate the determination of the ratio of sugars differing in configuration at C2.

***12.28** Bilinmeyen bir **X** bileşiği, infrared de 3200 - 3550 cm^{-1} de geniş bir soğurma bandı gösterir, fakat 1620-1780 bölgesinde band vermez. Bileşik sadece C, H ve O içerir.

116 mg'lık bir örnek, metilmagnezyum bromürün aşırısıyla etkileştirildiğinde, 20°C'da ve 750 mmHg'da civa üzerinde 48,7 mL metan gazı toplanmıştır.

X bileşiğin kütle spektrumunda en yüksek kütleli pik (zor belirlenebiliyor) 116 *m/z*'de ve başka bir parça piki de 98'de gözlenmektedir.

Bu bulgular **X** in yapısı hakkında hangi bilgileri verir?

***12.28** The IR indicates the presence of OH and absence of C=C and C=O. The MS indicates a molecular weight of 116 amu and confirms the presence of hydroxyl. The reaction data indicate X contains 2 protons per molecule that are acidic enough to react with a Grignard reagent, meaning two hydroxyl groups per molecule. (This analytical procedure, the Zerewitinoff determination, was routinely done before the advent of NMR.)

Thus X has a partial structure like:

$C_6H_{10}(OH)_2$ with one ring, or
$C_5H_6O(OH)_2$ with two rings, or (less likely)
$C_4H_2O_2(OH)_2$ with three rings.

Konjuge Doymamış Sistemler

13.5 REZONANS KURALLARININ ÖZETİ

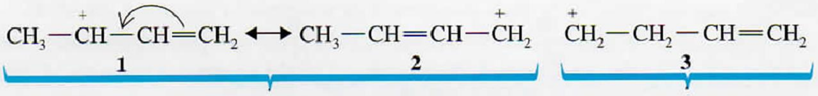
Rezonans, yapı ve tepkimeye girme kabiliyeti tartışıldığı zaman sık sık kullandığımız önemli bir araçtır.

Bu bölümün önceki kısımlarında, π bağlarındaki elektronların (ve yüklerin) dağılımı ile iyonları ve radikalleri tanımlarken rezonans teorisini oldukça çok kullanmıştık. Rezonans teorisi bu gibi sistemlerde oldukça faydalıdır ve biz bu teoriyi ilerideki bölümlerde tekrar tekrar kullanacağız. Altbölüm 1.8'de rezonans teorisine bir giriş yapmıştık ve şimdi o giriş, rezonans yapıların yazılması ve verilen bir yapının melez yapıya olan katkısının tahmin edilmesi için kuralları özetlerken yardımcı olacaktır.

13.5A Rezonans Yapıların Yazımı için Kurullar

1. **Rezonans yapılar sadece kağıt üzerinde vardır.** Rezonans yapılar gerçek olmamasına rağmen, tek bir Lewis yapısının yetersiz kaldığı durumlarda, iyon, radikal ve moleküllerin tanımlanmasında bize yardımcı olduklarından faydalıdırlar. Rezonans veya rezonansa katkıda bulunan yapılar olarak adlandırılan iki veya daha fazla Lewis yapısı yazabiliriz. Bu yapıları çift başlıklı ok (⟷) ile birleştiririz ve gerçek molekülün, radikalin veya iyonun, onların hepsinin bir melezi olduğunu söyleriz.

2. **Rezonans yapıların yazımında sadece elektronların hareketine izin veririz.** Atomların çekirdeklerinin yerleri yapıların hepsinde aynı kalmak zorundadır. Aşağıda verilen **3** yapısı, allil katyonu için bir rezonans yapı değildir, çünkü onu oluşturmak için bir hidrojen atomunu hareket ettirmek zorundayız ve buna da izin verilmez.



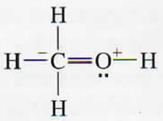
$$\underbrace{\underset{\mathbf{1}}{CH_3-\overset{+}{C}H-CH=CH_2} \longleftrightarrow \underset{\mathbf{2}}{CH_3-CH=CH-\overset{+}{C}H_2}} \qquad \underbrace{\underset{\mathbf{3}}{\overset{+}{C}H_2-CH_2-CH=CH_2}}$$

Bu yapılar 1,3-bütadienin bir proton aldığı zaman oluşan allil katyonu için rezonons yapılardır.

Bir hidrojen atomu yer değiştirdiğinden dolayı allilik katyon için uygun bir rezonons yapı değildir.

Genellikle, elektronları hareket ettirdiğimizde sadece π bağlarının elektronlarını (yukarıdaki örnekte olduğu gibi) ve serbest elektron çiftlerini hareket ettiririz.

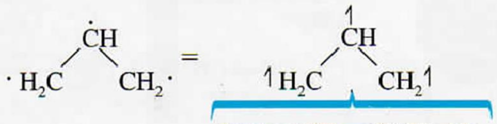
3. **Tüm yapılar Lewis yapılarına uygun olmalıdır.** Örneğin karbon atomu için beş bağa sahip olduğu yapılar yazılamaz.



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{-}{C}}}=\ddot{O}\overset{+}{-}H$$

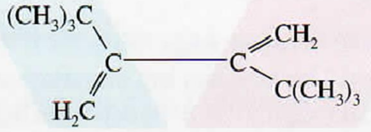
Karbon beş bağ yaptığından, bu, metanol için uygun bir rezonans yapısı değildir. Periyodik çizelgenin birinci sırasının (2. periyot) elementleri, değerlik kabuklarında sekiz elektrondan fazla bulunduramazlar.

4. Bütün rezonans yapılar aynı sayıda çiftleşmemiş elektrona sahip olmalıdır. Aşağıdaki yapı, üç tane elektron içerdiği için allil radikali için bir rezonans yapı değildir ve allil radikali sadece bir elektron bulundurur.



Bu yapı, $CH_2{=}CHCH_2\cdot$'de olduğu gibi aynı sayıda çiftleşmemiş elektron bulundurmadığı için allil radikali için uygun bir rezonons yapı değildir.

5. Delokalize olan sistemin tüm atomları aynı düzlemde veya düzlem yapıya çok yakın bir durumda olmak zorundadır. Örneğin 2,3-di-*ter*-bütil-1,3-bütadiende *ter*-bütil grupları çok hacimli gruplar olduğu için yapıyı döndürürler ve ikili bağın aynı düzlemde bulunabilmesini engellerler, bu yüzden bu bileşik *konjuge olmayan* bir dien gibi davranır. C2 ve C3'teki *p* orbitalleri aynı düzlemde olmadığı için örtüşmezler ve delokalizasyon (bundan dolayı rezonans) önlenir.

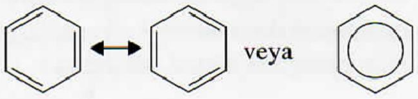


2,3-Di-*ter*-bütil-1,3-bütadien

6. Gerçek molekülün enerjisi katkıda bulunan rezonans yapılarından herhangi birisinin enerjisinden daha azdır. Örneğin, gerçek allil katyonu ayrı ayrı gösterilen **4** veya **5** rezonans yapılarının herhangi birinden daha kararlıdır. **4** ve **5** yapıları birincil karbokatyona benzer ve allil katyonu ikincil bir karbokatyondan daha kararlıdır (düşük enerjilidir). Kimyacılar sık sık kararlılığın bu çeşidini *rezonans kararlılığı* olarak adlandırırlar.

$$\underset{\mathbf{4}}{CH_2{=}CH{-}\overset{+}{C}H_2} \longleftrightarrow \underset{\mathbf{5}}{\overset{+}{C}H_2{-}CH{=}CH_2}$$

Bölüm 14'te, iki özdeş yapının melezi olan, bu nedenle çok fazla rezonans kararlılığına sahip olan benzeni inceleyeceğiz.

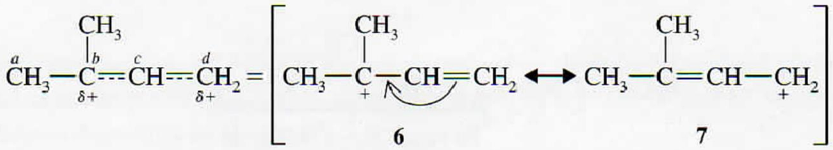


Benzenin rezonons yapıları **Melez gösterimi**

7. Eşdeğer rezonans yapılar meleze eşit katkılarda bulunur ve bunların temsil ettiği bir sistem büyük bir rezonans kararlılığına sahiptir. **4** ve **5** yapıları eşdeğer olduğu için allil katyonuna katkıları eşit olur. Allil katyonunun alışılmamış ölçüde kararlı olması da bu özdeş rezonans yapıların çok büyük kararlılık katkısı yapmasıyla açıklanabilir. Aynı şeyler benzenin eşdeğer yapıları ve allil radikalinin eşdeğer **A** ve **B** yapıları (Altbölüm 13.3B) tarafından yapılan katkılar için de söylenebilir.

8. Bir yapı ne kadar kararlı ise (kendisi ele alındığında) meleze katkısı o kadar büyüktür. Eşdeğer olmayan yapılar eşit katkı yapmazlar. Örneğin, aşağıdaki katyon, **6**

ve **7** yapılarının bir melezidir. **6** yapısı **7** yapısından daha fazla bir katkı yapar, çünkü **7** yapısı bir birincil karbokatyon iken **6** yapısı daha kararlı bir üçüncül karbokatyondur.



$$\overset{a}{CH_3}-\underset{\delta+}{\overset{\overset{CH_3}{|\,b}}{C}}\overset{c}{\cdots CH}\cdots\underset{\delta+}{\overset{d}{C}H_2} = \left[CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \longleftrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH-\underset{+}{C}H_2\right]$$

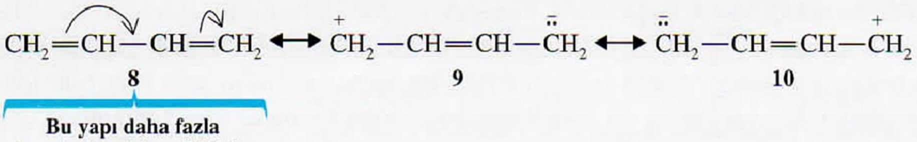
6 **7**

6 yapısının daha büyük bir katkıda bulunmasının anlamı, melezin *b* karbonu üzerindeki kısmî pozitif yükün *d* karbonu üzerindeki kısmi pozitif yükten daha büyük olabileceğidir. Aynı zamanda bunun anlamı, *c* ve *d* karbon atomları arasındaki bağın *b* ve *c* karbon atomları arasındaki bağdan daha fazla ikili bağa benzeyebileceğidir.

13.5B Rezonans Yapıların Bağıl Kararlılıklarının Tahmin Edilmesi

Aşağıdaki kurallar, rezonans yapıların bağıl kararlılıkları hakkında karar vermemize yardımcı olacaktır.

a. Bir yapı ne kadar çok kovalent bağa sahip ise o kadar kararlıdır. Bu tamamen beklenen durumdur, çünkü bir kovalent bağ oluşurken atomların enerjisi düşer. 1,3-Bütadien için verilen aşağıdaki yapılardan **8**, birden fazla bağ ihtiva ettiği için en büyük katkı yapan ve en kararlı olandır. (Aynı zamanda altta verilecek olan **c** kuralına göre daha kararlıdır.)

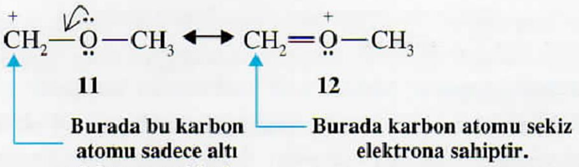


$$CH_2=CH-CH=CH_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH-\ddot{C}H_2 \longleftrightarrow \ddot{C}H_2-CH=CH-\overset{+}{C}H_2$$

8 **9** **10**

Bu yapı daha fazla kovalent bağ içerdiği için en kararlıdır.

b. Değerlik kabukları tamamen elektronlarla dolu olan (yani soy gaz yapısında) atomlardan oluşan yapılar özellikle kararlıdır ve meleze büyük katkı yaparlar. Bu sonuç, bağlanma hakkında bildiklerimize göre beklememiz gereken bir sonuçtur. Örneğin, **12** yapısı, bütün atomlarının değerlik kabukları dolu olduğundan **11** yapısına göre aşağıdaki katyonun kararlılığına daha büyük katkı sağlar. (**12** yapısının **11**'den çok daha fazla kovalent bağa sahip olduğuna dikkat ediniz; bkz. kural **a**).



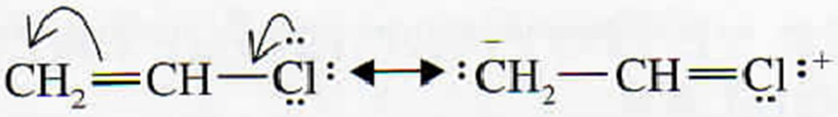
$$\overset{+}{C}H_2-\underset{..}{\ddot{O}}-CH_3 \longleftrightarrow CH_2=\overset{+}{\underset{..}{O}}-CH_3$$

11 **12**

Burada bu karbon atomu sadece altı elektrona sahiptir.

Burada karbon atomu sekiz elektrona sahiptir.

c. Yük ayrımı kararlılığı azaltır. Zıt yükleri ayırmak enerji gerektirir. Bu yüzden zıt yüklü yapılar yük ayrımı olmamış olanlardan daha büyük enerjiye sahiptir (daha az kararlıdır). Vinil klorürün aşağıdaki iki yapısından **13** yapısında yük ayrımı olmadığı için yapıya katkısı çok büyüktür. (Bu, **14** yapısı meleze katkı yapmaz anlamında değildir, 14 yapısının katkısını çok az olduğunu ifade eder.)



$$CH_2=CH-\underset{..}{\ddot{Cl}}: \longleftrightarrow :\overset{-}{C}H_2-CH=\underset{..}{Cl}:^{+}$$

13 **14**

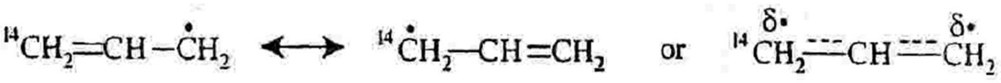
Problem 13.1 ➤ (a) Birinci karbonu ${}^{14}C$ olarak işaretlenmiş propen, allilik klorlamaya veya bromlamaya maruz bırakıldığında hangi ürünün (ürünlerin) oluşacağını umarsınız? (b) Cevabınızı açıklayınız.

$$^{14}CH_2{=}CHCH_3 + X_2 \xrightarrow[\text{düşük derişimde } X_2]{\text{yüksek sıcaklık} \atop \text{veya}} ?$$

(c) Birden daha fazla ürün elde edilirse, bunların bağıl oranlarının nasıl olmasını beklersiniz?

13.1 (a) $^{14}CH_2{=}CHCH_2X$ and $CH_2{=}CH{-}\overset{14}{C}H_2X$

(b) The reaction proceeds through the resonance-stabilized radical.



$$^{14}CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow {}^{14}\dot{C}H_2{-}CH{=}CH_2 \quad \text{or} \quad {}^{14}\overset{\delta\bullet}{C}H_2\text{---}CH\text{---}\overset{\delta\bullet}{C}H_2$$

Thus, attack on X_2 can occur by the carbon atom at either end of the chain since these atoms are equivalent.

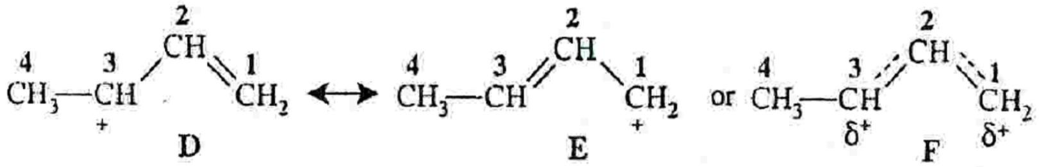
(c) 50:50 because attack at the two ends of the chain is equally probable.

Problem 13.2 ➤ (a) Aşağıda verilen karbokatyon için **D**, **E** ve **F**'ye karşılık gelen yapıları yazınız.

$$CH_3{-}\overset{+}{C}H{-}CH{=}CH_2$$

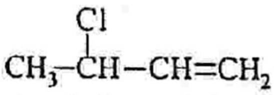
(b) Bu karbokatyonun, bir üçüncül karbokatyondan bile daha kararlı olduğu görülür; bunu nasıl açıklarsınız. (c) Bu karbokatyon klor iyonu ile tepkimeye girerse hangi ürünün (ürünlerin) oluşmasını beklersiniz?

13.2 (a)



(b) We know that the allylic cation is almost as stable as a tertiary carbocation. Here we find not only the resonance stabilization of an allylic cation but also the additional stabilization that arises from contributor **D** in which the plus charge is on a secondary carbon atom.

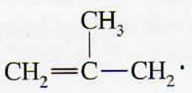
(c)



$CH_3{-}\underset{}{\overset{Cl}{\overset{|}{C}}}H{-}CH{=}CH_2$ and $CH_3{-}CH{=}CH{-}CH_2{-}Cl$, because the Cl will attack the chain at the two positive centers shown in structure **F**.

Aşağıdakilerin her biri için önemli olan rezonans yapıları yazınız. ◀ **Problem 13.3**

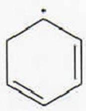
(a)



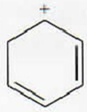
$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2\cdot$

(b) $CH_2{=}CH{-}\underset{+}{C}H{-}CH{=}CH_2$

(c)



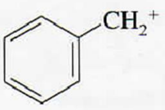
(d)



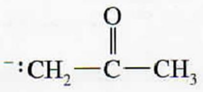
(e) $CH_3CH{=}CH{-}CH{=}\overset{+}{\ddot{O}}H$

(f) $CH_2{=}CH{-}Br$

(g)



(h)

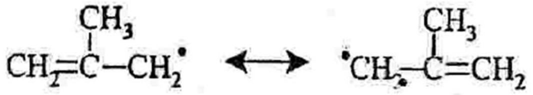


$^{-}\!:CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$

(i) $CH_3{-}S{-}CH_2^{+}$

(j) $CH_3{-}NO_2$

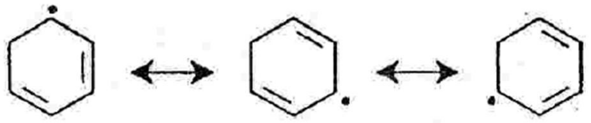
13.3 (a)



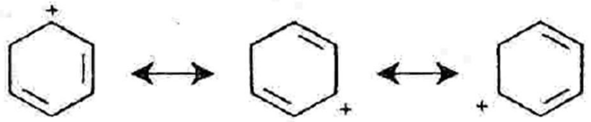
$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2^{\bullet}} \longleftrightarrow \mathrm{{}^{\bullet}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2}$

(b) $\mathrm{CH_2{=}CH{-}\underset{+}{C}H{-}CH{=}CH_2} \longleftrightarrow \mathrm{{}^{+}CH_2{-}CH{=}CH{-}CH{=}CH_2} \longleftrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}\overset{+}{C}H_2}$

(c)



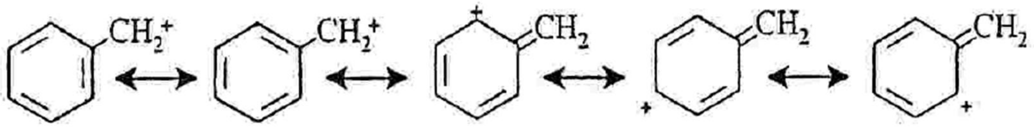
(d)



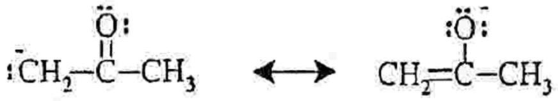
(e) $\mathrm{CH_3CH{=}CH{-}CH{=}\overset{+}{\underset{\cdot\cdot}{O}}H} \longleftrightarrow \mathrm{CH_3CH{=}CH{-}\overset{+}{C}H{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H} \longleftrightarrow \mathrm{CH_3\overset{+}{C}H{-}CH{=}CH{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}H}$

(f) $\mathrm{CH_2{=}CH{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}{:}} \longleftrightarrow \mathrm{{:}CH_2{-}CH{=}\overset{\cdot\cdot+}{Br}{:}}$

(g)



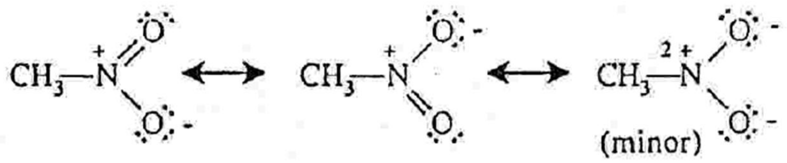
(h)



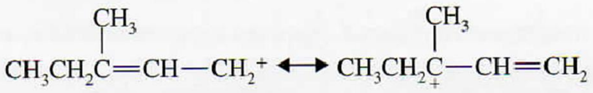
$\mathrm{{:}\bar{C}H_2{-}\overset{\ddot{O}{:}}{\overset{\|}{C}}{-}CH_3} \longleftrightarrow \mathrm{CH_2{=}\overset{{:}\ddot{O}{:}^{-}}{\overset{|}{C}}{-}CH_3}$

(i) $\mathrm{CH_3{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}{-}CH_2^{+}} \longleftrightarrow \mathrm{CH_3{-}\overset{+}{\underset{\cdot\cdot}{S}}{=}CH_2}$

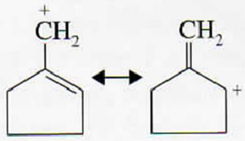
(j)



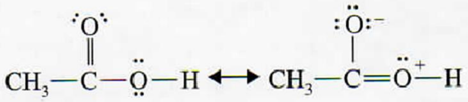
Aşağıdaki rezonans yapıların her birisinin meleze en büyük katkıda bulunanını seçiniz ve seçiminizi açıklayınız. ◄ **Problem 13.4**

(a)


$CH_3CH_2\overset{CH_3}{\overset{|}{C}}=CH-CH_2^+ \leftrightarrow CH_3CH_2\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH=CH_2$

(b)


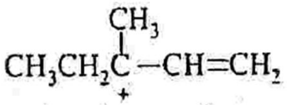
(c) $\overset{+}{C}H_2-\ddot{N}(CH_3)_2 \leftrightarrow CH_2=\overset{+}{N}(CH_3)_2$

(d)


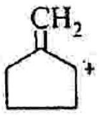
$CH_3-\overset{\ddot{O}}{\overset{\|}{C}}-\ddot{O}-H \leftrightarrow CH_3-\overset{:\ddot{O}:^-}{\overset{|}{C}}=\ddot{O}^+-H$

(e) $\underset{\cdot}{C}H_2CH=CHCH=CH_2 \leftrightarrow CH_2=CH\underset{\cdot}{C}HCH=CH_2 \leftrightarrow CH_2=CHCH=CH\underset{\cdot}{C}H_2$

(f) $:NH_2-C\equiv N: \leftrightarrow \overset{+}{N}H_2=C=\ddot{N}:^-$

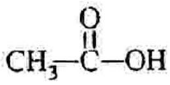
13.4 (a)


$CH_3CH_2\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH=CH_2$ because the positive charge is on a tertiary carbon atom rather than a primary one (rule 8).

(b)


because the positive charge is on a secondary carbon atom rather than a primary one (rule 8).

(c) $CH_2=\overset{+}{N}(CH_3)_2$ because all atoms have a complete octet (rule 8b), and there are more covalent bonds (rule 8a).

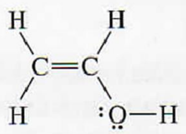
(d)


$CH_3-\overset{O}{\overset{\|}{C}}-OH$ because it has no charge separation (rule 8c).

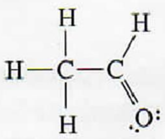
(e) $CH_2=CH\dot{C}HCH=CH_2$ because the radical is on a secondary carbon atom rather than a primary one (rule 8).

(f) $:NH_2-C\equiv N:$ because it has no charge separation (rule 8c).

Aşağıdaki keto ve enol yapılarında elektronların yerleri farklıdır, fakat bu yapılar rezonans yapılar değildir. Niçin? Açıklayınız. ◄ **Problem 13.5**



Enol yapısı



Keto yapısı

13.5 In resonance structures, the positions of the nuclei must remain the same for all structures (rule 2). The keto and enol forms shown differ not only in the positions of their electrons, but also in the position of one of the hydrogen atoms. In the enol form, it is attached to an oxygen atom; in the keto form, it has been moved so that it is attached to a carbon atom.

(a) Bölüm 13.6'daki bileşiklerin hangileri konjuge diendir? (b) Hangi bileşik izole bir diendir? (c) Hangi bileşik bir izole enindir? ◄ **Problem 13.6**

13.6 (a) *cis*-1,3-Pentadiene, *trans,trans*-2,4-hexadiene, *cis,trans*-2,4-hexadiene, and 1,3-cyclohexadiene are conjugated dienes.

(b) 1,4-Cyclohexadiene and 1,4-pentadiene are isolated dienes.

(c) 1-Penten-4-yne is an isolated enyne.

Problem 13.7

İki bileşik, **A** ve **B**, aynı molekül formülüne sahiptir, C_6H_8. **A** ve **B**'nin her ikisi de sikloheksan vermek üzere platin varlığında hidrojenin iki eşdeğer molü ile tepkimeye girer. **A** bileşiği genişband eşleşmesiz ^{13}C NMR spektrumunda üç sinyal verir. **B** bileşiği ise sadece iki ^{13}C NMR sinyali gösterir. **A** bileşiği 256 nm'de bir soğurma maksimumuna sahiptir, buna karşın **B** bileşiği 200 nm'den daha uzun dalga boyunda hiç bir soğurma göstermez. **A** ve **B**'nin yapısı nedir?

13.7 The formula, C_6H_8, tells us that A and B have six hydrogen atoms less than an alkane. This unsaturation may be due to three double bonds, one triple bond and one double bond, or combinations of two double bonds and a ring, or one triple bond and a ring. Since both A and B react with 2 mol of H_2 to yield cyclohexane, they are either cyclohexyne or cyclohexadienes. The absorption maximum of 256 nm for A tells us that it is conjugated. Compound **B**, with no absorption maximum beyond 200 nm, possesses isolated double bonds. We can rule out cyclohexyne because of ring strain caused by the requirement of linearity of the $-C\equiv C-$ system. Therefore, A is 1,3-cyclohexadiene; B is 1,4-cyclohexadiene.

Problem 13.8

Üç bileşik, **D**, **E** ve **F**, C_5H_6 molekül formülüne sahiptir. Üç bileşiğin hepsi de platin varlığında 3 eşdeğer mol hidrojen soğurur ve pentan oluşturur. **E** ve **F** bileşikleri yaklaşık olarak 3300 cm^{-1}'de bir İR soğurmasına sahiptir. **D** bileşiği ise bu bölgede İR absorbsiyonuna sahip değildir. **D** ve **E** bileşikleri UV – Vis spektrumlarında 230 nm yakınlarında bir maksimum soğurma gösterir. **F** bileşiği 200 nm'nin ötesinde maksimum soğurma göstermez. **D**, **E** ve **F** için yapılar öneriniz.

13.8 All three compounds have an unbranched five-carbon chain, because the product of hydrogenation is unbranched pentane. The formula, C_5H_6, suggests that they have one double bond and one triple bond. Compounds **D, E,** and **F** must differ, therefore, in the way the multiple bonds are distributed in the chain. Compounds E and F have a terminal $-C\equiv CH$ [IR absorption at ~3300 cm^{-1}]. The UV absorption maximum near 230 nm for **D** and **E** suggests that in these compounds, the multiple bonds are conjugated. The structures are

$CH_3-C\equiv C-CH=CH_2$ **D**

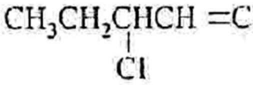
$HC\equiv C-CH=CH-CH_3$ **E**

$HC\equiv C-CH_2-CH=CH_2$ **F**

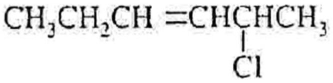
Problem 13.9

(a) Hidrojen klorür 2,4-heksadien ($CH_3CH=CHCH=CHCH_3$) ile, (b) 1,3-pentadien, ($CH_2=CHCH=CHCH_3$) ile tepkimeye girdiği zaman elde edilmesi beklenen ürünler neler olacaktır? (cis,trans izomerisini ihmal ediniz.)

13.9 (a) Recall that 1,2 and 1,4 addition refer to the conjugated system itself and not the entire carbon chain.


$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH{=}CHCH_3$

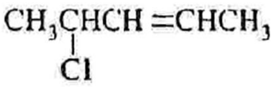
and


$CH_3CH_2CH{=}CH\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$

(b) The most stable cation is a hybrid of equivalent forms:

$$CH_3\overset{+}{C}HCH{=}CHCH_3 \longleftrightarrow CH_3CH{=}CH\overset{+}{C}HCH_3$$

Thus, 1,4 and 1,2 addition yield the same product.


$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH{=}CHCH_3$

Problem 13.10 (a) 1,3-Bütadien ile hidrojen bromürün 1,2-katılma tepkimesinin, 1,4-katılma tepkimesinden daha hızlı oluştuğunu gösteren muhtemel bir açıklama önerebilir misiniz? (*İpucu*: Allilik katyonun rezonans melezini oluşturan $CH_3\overset{+}{C}HCH{=}CH_2$ ve $CH_3CH{=}CH\overset{+}{C}H_2$ yapılarının bağıl katkısını göz önünde bulundurunuz.) (b) 1,4-katılma ürününün daha kararlı olmasını nasıl açıklarsınız?

13.10 Addition of the proton gives the resonance hybrid.

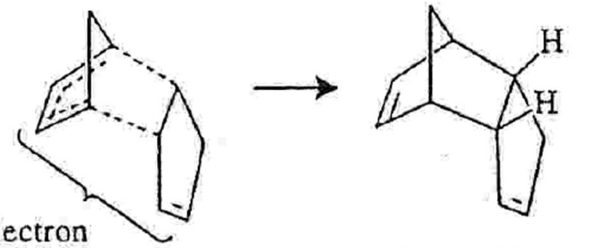
$$\text{(a)}\quad \underset{\textbf{I}}{CH_3{-}\overset{+}{C}H{-}CH{=}CH_2} \longleftrightarrow \underset{\textbf{II}}{CH_3{-}CH{=}CH{-}\overset{+}{C}H_2}$$

The inductive effect of the methyl group in **I** stabilizes the positive charge on the adjacent carbon. Such stabilization of the positive charge does not occur in **II**. Because **I** contributes more heavily to the resonance hybrid than does **II**, C2 bears a greater positive charge and reacts faster with the bromide ion.

(b) In the 1,4-addition product, the double bond is more highly substituted than in the 1,2-addition product; hence it is the more stable alkene.

Problem 13.11 ➤ Siklopentadienin dimerleşmesi de endo şeklinde oluşur. (a) Bunun nasıl olduğunu gösteriniz. (b) Hangi π elektronları etkileşir? (c) Ürünün üç boyutlu yapısı nasıldır?

13.11 (a), (c)



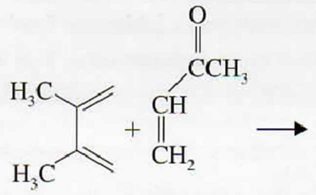
(b) π-Electron interaction occurs here.

Endo adduct

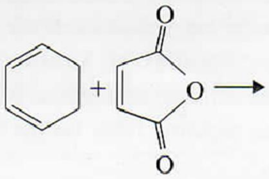
Aşağıdaki tepkimelerden beklediğiniz ürünler nelerdir?

Problem 13.12

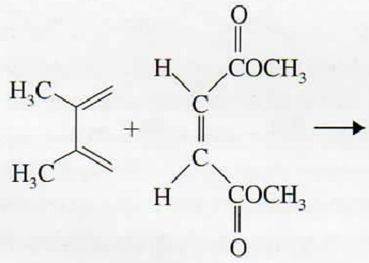
(a)



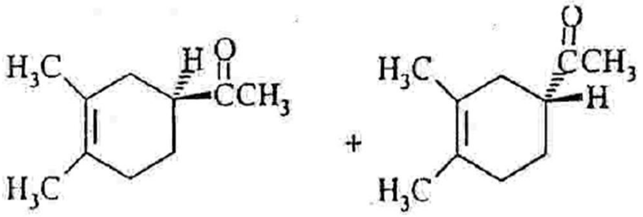
(c)



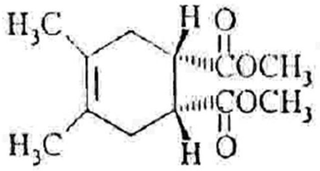
(b)



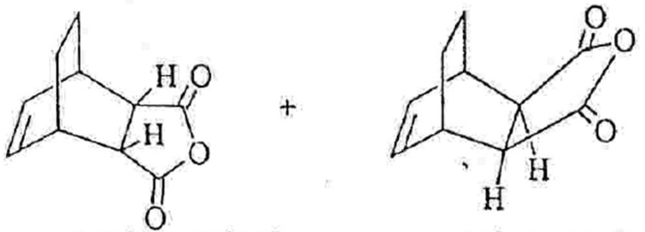
13.12 (a)



(b)



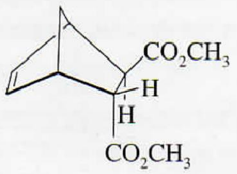
(c)



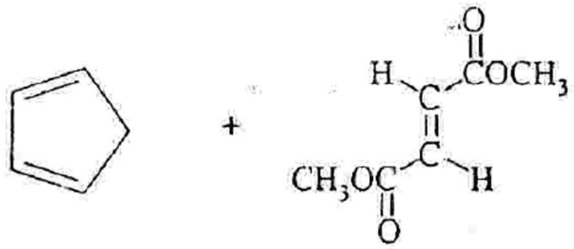
(major product) (minor product)

Aşağıdaki bileşiği sentezlemek için hangi dien ve dienofili kullanırsınız?

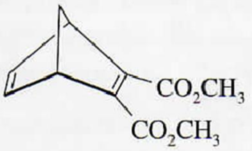
Problem 13.13



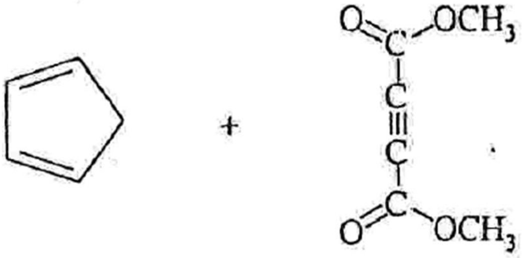
13.13 Use the trans diester because the stereochemistry is retained in the adduct.



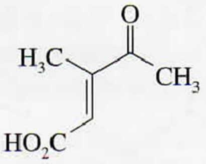
Problem 13.14 ➤ Diels – Alder tepkimeleri üç bağlı (asetilenik) dienofillerle de oluşur. Aşağıdaki bileşiği hazırlamak için hangi dien ve dienofili kullanırsınız?



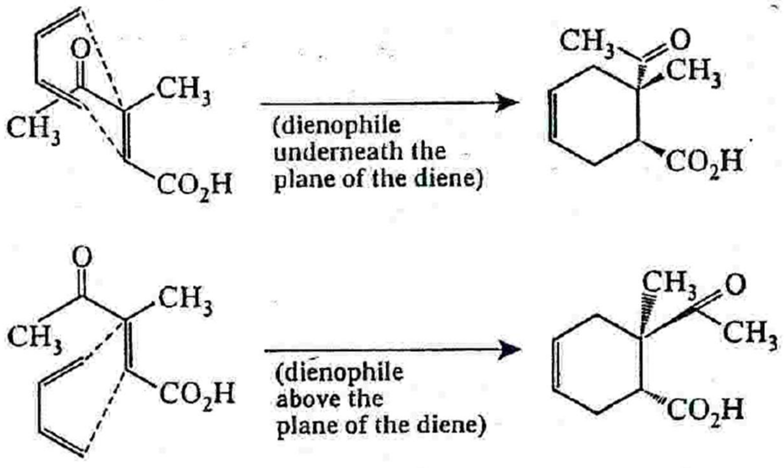
13.14



Problem 13.15 ➤ 1,3-Bütadien ve aşağıda gösterilen dienofil, B_{12} vitaminin sentezinde A. Eschenmoser ve R. B. Woodword tarafından kullanılmıştır. Bu tepkimede oluşabilecek Diels – Alder enantiyomerlerinin yapısını çiziniz ve onların oluşumuna yol açan iki geçiş durumunu gösteriniz.



13.15


O
CH₃
CH₃
CO₂H
(dienophile underneath the plane of the diene)
CH₃
O
CH₃
CO₂H
O
CH₃
CH₃
CO₂H
(dienophile above the plane of the diene)
CH₃
O
CH₃
CO₂H

(Or, in each case, the other face of the dienophile could present itself to the diene, resulting in the respective enantiomer.)

13.16 Aşağıdakilerden çıkarak 1,3-bütadienin sentezini tasarlayınız.

(a) 1,4-Dibromobütan

(b) $HOCH_2(CH_2)CH_2OH$

(c) $CH_2{=}CHCH_2CH_2OH$

(d) $CH_2{=}CHCH_2CH_2Cl$

(e) $CH_2{=}CHCHClCH_3$

(f) $CH_2{=}CHCH(OH)CH_3$

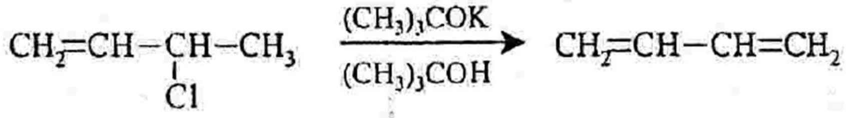
(g) $HC{\equiv}CCH{=}CH_2$

13.16 (a) $BrCH_2CH_2CH_2CH_2Br \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

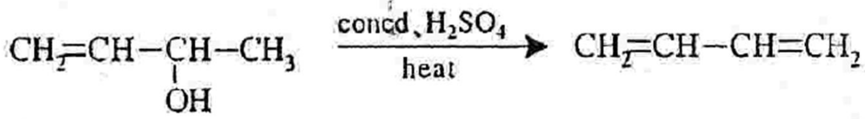
(b) $HOCH_2CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{concd } H_2SO_4} CH_2{=}CH{-}CH{=}CH_2$

(c) $CH_2{=}CH{-}CH_2CH_2{-}OH \xrightarrow[\text{heat}]{\text{concd } H_2SO_4} CH_2{=}CH{-}CH{=}CH_2$

(d) $CH_2{=}CH{-}CH_2CH_2{-}Cl \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

(e) 

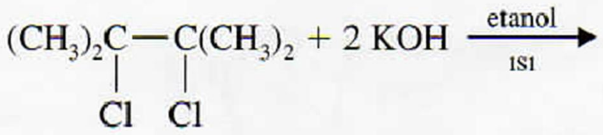
$CH_2{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{C}H}{-}CH_3 \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$

(f) 

$CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3 \xrightarrow[\text{heat}]{\text{concd}.\, H_2SO_4} CH_2{=}CH{-}CH{=}CH_2$

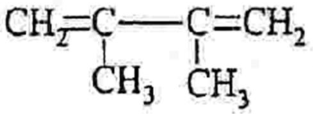
(g) $CH_2{=}CH{-}C{\equiv}CH \;+\; H_2 \xrightarrow{Ni_2B\ (P\text{-}2)} CH_2{=}CH{-}CH{=}CH_2$

13.17 Aşağıdaki tepkimede hangi ürünün oluşmasını beklersiniz?



$$(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}{-}\underset{\displaystyle Cl}{\underset{|}{C}}(CH_3)_2 + 2\,KOH \xrightarrow[\text{ısı}]{\text{etanol}}$$

13.17

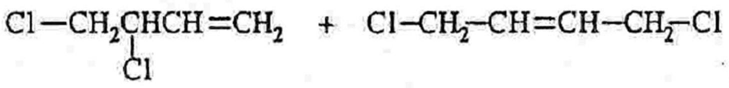


$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

13.18 Aşağıdaki reaktiflerin her biri ile 1,3-bütadienin 1 molünün tepkimesinden hangi ürünlerin oluşmasını beklersiniz? (Eğer tepkime olmuyorsa o şekilde belirtiniz.)

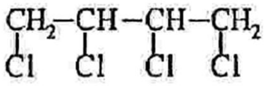
(a) Bir mol Cl_2
(b) İki mol Cl_2
(c) İki mol Br_2
(d) İki mol H_2, Ni
(e) H_2O da bir mol Cl_2
(f) Sıcak $KMnO_4$
(g) H_2SO_4, H_2O

13.18 (a)



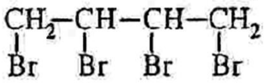
$$\mathrm{Cl-CH_2\underset{Cl}{\underset{|}{C}}HCH=CH_2 \;+\; Cl-CH_2-CH=CH-CH_2-Cl}$$

(b)



$$\mathrm{\underset{Cl}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}}$$

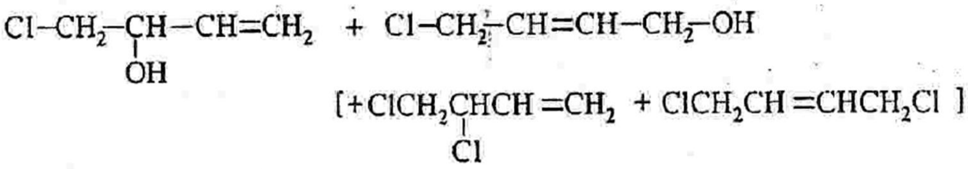
(c)



$$\mathrm{\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}}$$

(d) $\mathrm{CH_3-CH_2-CH_2-CH_3}$

(e)

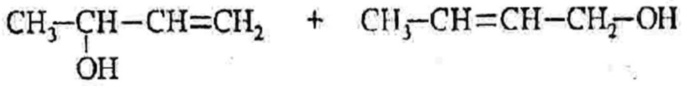


$$\mathrm{Cl-CH_2-\underset{OH}{\underset{|}{CH}}-CH=CH_2 \;+\; Cl-CH_2-CH=CH-CH_2-OH}$$

$$\mathrm{[+ClCH_2\underset{Cl}{\underset{|}{C}}HCH=CH_2 \;+\; ClCH_2CH=CHCH_2Cl\;]}$$

(f) 4 CO_2 (*Note:* $KMnO_4$ oxidizes HO_2C-CO_2H to 2 CO_2)

(g)



$$\mathrm{CH_3-\underset{OH}{\underset{|}{CH}}-CH=CH_2 \;+\; CH_3-CH=CH-CH_2-OH}$$

13.19 Aşağıdaki dönüşümlerin her birinin nasıl gerçekleşebileceğini gösteriniz. (Bazı dönüşümlerde birkaç basamak gerekebilir.)

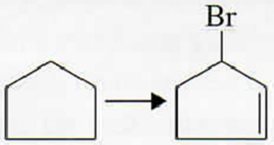
(a) 1-Büten ⟶ 1,3-bütadien

(b) 1-Penten ⟶ 1,3-pentadien

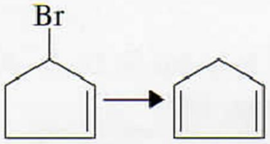
(c) $\mathrm{CH_3CH_2CH_2CH_2OH \longrightarrow CH_2BrCH{=}CHCH_2Br}$

(d) $\mathrm{CH_3CH{=}CHCH_3 \longrightarrow CH_3CH{=}CHCH_2Br}$

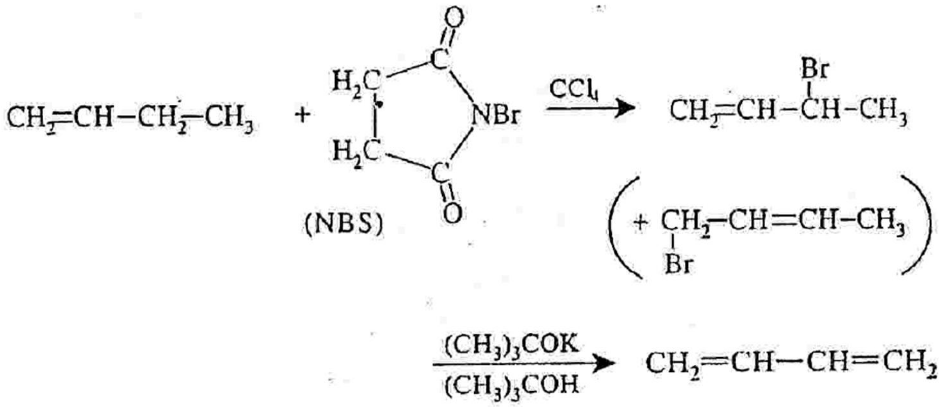
(e)



(f)



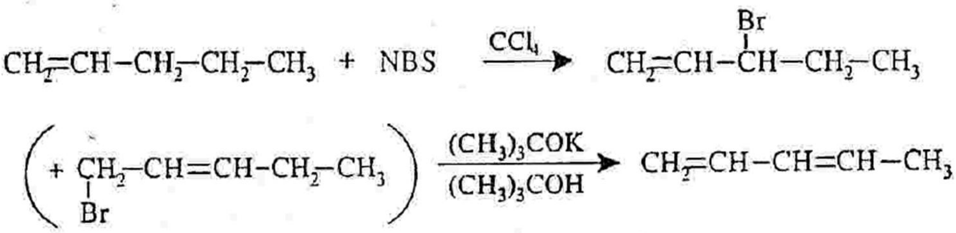
13.19 (a)



$$CH_2{=}CH{-}CH_2{-}CH_3 + NBS \xrightarrow{CCl_4} CH_2{=}CH{-}\overset{Br}{\overset{|}{C}}H{-}CH_3 \quad \left(+\ \underset{\underset{Br}{|}}{C}H_2{-}CH{=}CH{-}CH_3\right) \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH_2$$

Note: In the second step, both allylic halides undergo elimination of HBr to yield 1,3-butadiene; therefore, separating the mixture produced in the first step is unnecessary. The $BrCH_2CH{=}CHCH_3$ undergoes a 1,4 elimination (the opposite of a 1,4 addition).

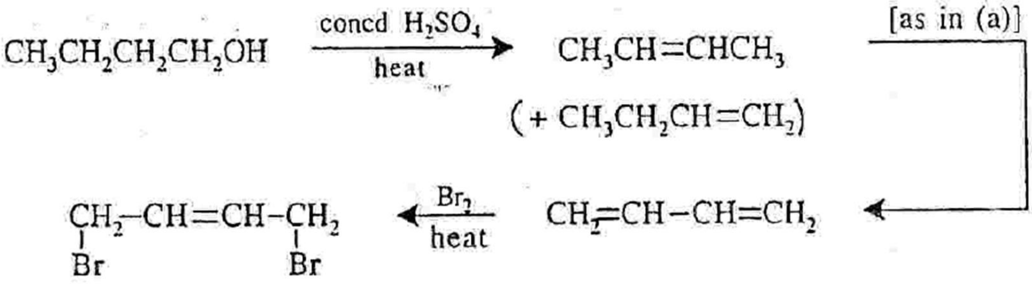
(b)



$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3 + NBS \xrightarrow{CCl_4} CH_2{=}CH{-}\overset{Br}{\overset{|}{C}}H{-}CH_2{-}CH_3 \quad \left(+\ \underset{\underset{Br}{|}}{C}H_2{-}CH{=}CH{-}CH_2{-}CH_3\right) \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} CH_2{=}CH{-}CH{=}CH{-}CH_3$$

Here again both products undergo elimination of HBr to yield 1,3-pentadiene.

(c)

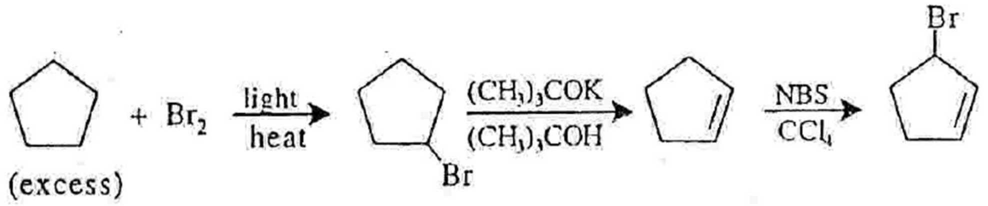


$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{concd } H_2SO_4} CH_3CH{=}CHCH_3 \ (+\ CH_3CH_2CH{=}CH_2) \xrightarrow{\text{[as in (a)]}} CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{heat}]{Br_2} \underset{\underset{Br}{|}}{C}H_2{-}CH{=}CH{-}\underset{\underset{Br}{|}}{C}H_2$$

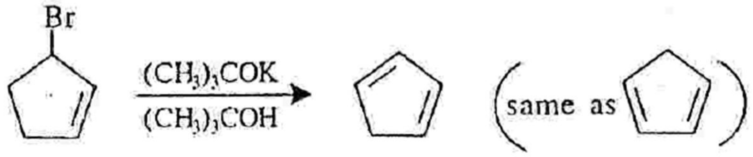
(d) $CH_3{-}CH{=}CH{-}CH_3 + NBS \xrightarrow{CCl_4} CH_3{-}CH{=}CH{-}CH_2Br$

$+\ CH_2{=}CH{-}CHBr{-}CH_3$

(e)

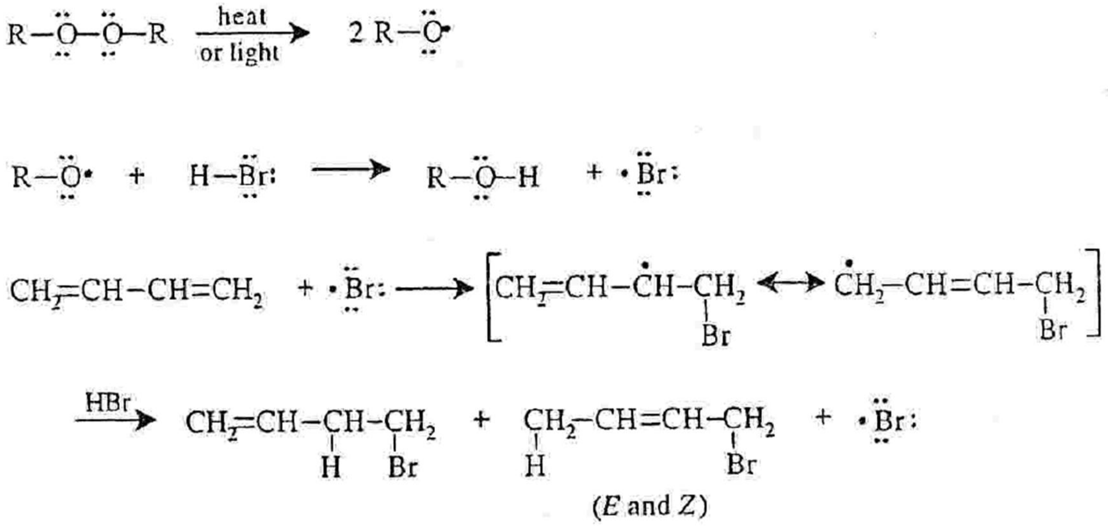


(f)



13.20 Konjuge dienler serbest radikaller ile 1,2 ve 1,4 katılma tepkimesinin her ikisini de verirler. Buna göre, bir örnek olarak, peroksitli ortamda 1,3-bütadiene HBr'nin bir eşdeğer molünün katılmasını gösteriniz.

13.20



$$R-\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}-R \xrightarrow[\text{or light}]{\text{heat}} 2\,R-\ddot{\underset{..}{O}}\cdot$$

$$R-\ddot{\underset{..}{O}}\cdot + H-\ddot{\underset{..}{Br}}: \longrightarrow R-\ddot{\underset{..}{O}}-H + \cdot\ddot{\underset{..}{Br}}:$$

$$CH_2=CH-CH=CH_2 + \cdot\ddot{\underset{..}{Br}}: \longrightarrow \left[CH_2=CH-\dot{C}H-\underset{Br}{CH_2} \longleftrightarrow \dot{C}H_2-CH=CH-\underset{Br}{CH_2}\right]$$

$$\xrightarrow{HBr} CH_2=CH-\underset{H}{CH}-\underset{Br}{CH_2} + \underset{H}{CH_2}-CH=CH-\underset{Br}{CH_2} + \cdot\ddot{\underset{..}{Br}}:$$

(*E* and *Z*)

13.21 UV–Vis, İR, NMR ve kütle spektrometresi spektroskopik aletlerdir ve bileşikler hakkında yapısal bilgileri elde etmek için kullanırız. Aşağıdaki bileşik çiftlerinden, bir çiftteki bir bileşiği diğerinden ayırdedebilecek bir spektroskopik yöntem (UV – Vis, İR, NMR ya da kütle spektroskopisi) belirtiniz.

(a) 1,3-Bütadien ve 1-bütün

(b) 1,3-Bütadien ve bütan

(c) Bütan ve $CH_2{=}CHCH_2CH_2OH$

(d) 1,3-Bütadien ve $CH_2{=}CHCH_2CH_2Br$

(e) $CH_2BrCH{=}CHCH_2Br$ ve $CH_3CBr{=}CBrCH_3$

13.21 Various IR, ^{1}H NMR, ^{13}C NMR, and MS features could be used to differentiate the members of any of these pairs. IR absorptions can be used to indicate whether double or triple bonds are present in a given molecule, or whether a hydroxyl group or halogen is present. Chemical shifts in the proton and carbon NMR spectra indicated can also be used to indicate the hybridization state of carbon atoms. The number of signals in the proton or carbon NMR spectrum for a given compound can suggest whether there is symmetry to the structure or not. Splitting patterns in the proton spectra can give detailed information about the connectivity of atoms. Mass spectra will indicate molecular weight differences when the molecular ions are present. Fragmentation patterns can indicate specific aspects of molecular structure characteristic to one member of a pair or another. UV would distinguish members of a pair where one is conjugated and the other is not. Consult tables with representative spectral information to predict specific aspects of the spectra for each compound.

13.22 **(a)** 1,4-Pentadienin C3'üne bağlanan hidrojen atomları nadiren radikaller tarafından çıkarılabilir. Bu durumu nasıl açıklarsınız? **(b)** 1,4-Pentadienin C3'üne bağlanan protonların propenin metil hidrojen atomlarından daha asidik olacağı gerçeğine bir açıklama getirebilir misiniz?

13.22 (a) Because a highly resonance-stabilized radical is formed:

$$CH_2{=}CH{-}\dot{C}H{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH{-}CH{=}CH_2$$

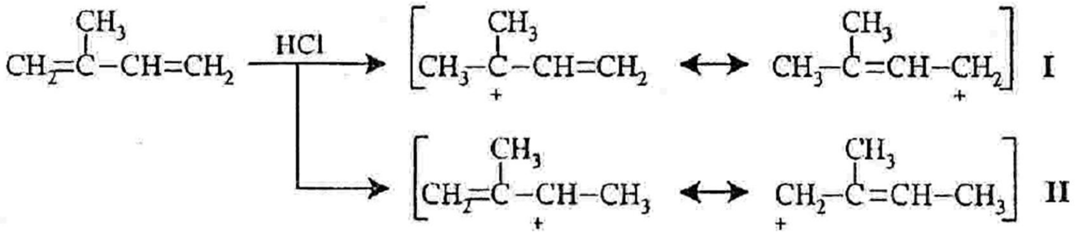
(b) Because the carbanion is more stable:

$$CH_2{=}CH{-}\overset{-}{\ddot{C}}H{-}CH{=}CH_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH{-}\overset{-}{\ddot{C}}H_2 \longleftrightarrow \overset{-}{\ddot{C}}H_2{-}CH{=}CH{-}CH{=}CH_2$$

That is, we can write more reasonance structures of nearly equal energies.

13.23 2-Metil-1,3-bütadien (izopren) hidrojen klorür ile 1,4 katılması verdiğinde ana ürün 1-kloro-3-metil-2-bütendir. 1-Kloro-2-metil-2-büten ya çok az oluşur ya da hiç oluşmaz. Bu durumu nasıl açıklayabilirsiniz?

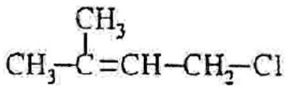
13.23



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \xrightarrow{HCl} \left[CH_3{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH_2 \longleftrightarrow CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}\underset{+}{CH_2}\right] \quad \text{I}$$

$$\longrightarrow \left[CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\underset{+}{CH}{-}CH_3 \longleftrightarrow \underset{+}{CH_2}{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3\right] \quad \text{II}$$

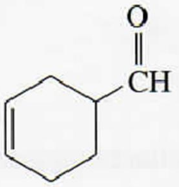
The resonance hybrid, I, has the positive charge, in part, on the tertiary carbon atom; in II, the positive charge is on primary and secondary carbon atoms only. Therefore, hybrid I is more stable and will be the intermediate carbocation. A 1,4 addition to I gives



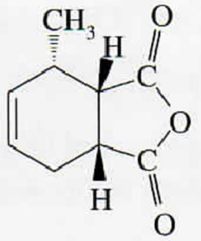
$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}Cl$$

13.24 Aşağıdakilerin her birinin sentezinde, hangi dien ve dienofili kullanırsınız?

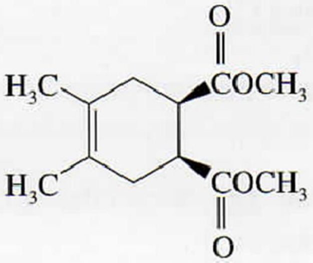
(a)



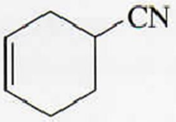
(d)



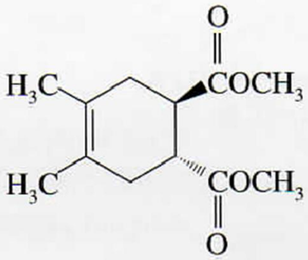
(b)



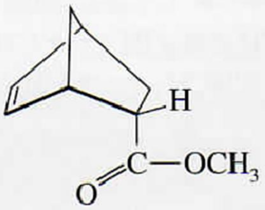
(e)



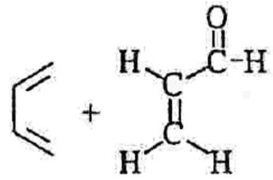
(c)



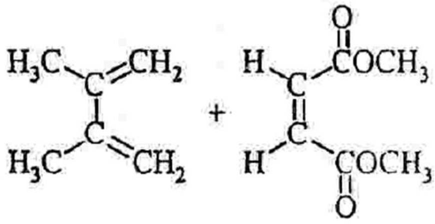
(f)



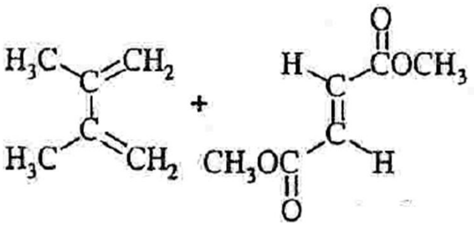
13.24 (a)



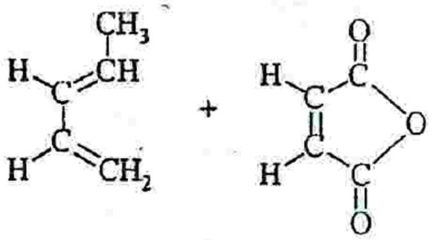
(b)



(c)



(d)



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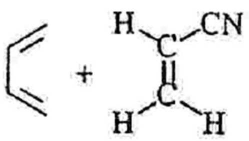

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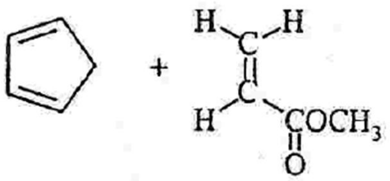
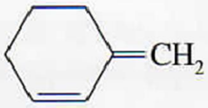
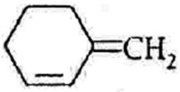


13.25 Aşağıdaki bileşiklerin her ikisinin de maleik anhidrit ile Diels–Alder tepkimesi veremeyecek olmalarının sebebini açıklayınız.

$HC\equiv C-C\equiv CH$ veya

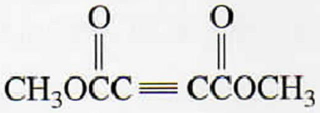


13.25 Neither compound can assume the s-cis conformation. 1,3-Butadiyne is linear, and



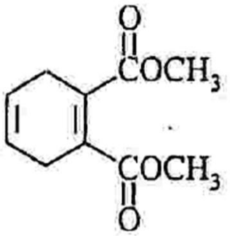
is held in an s-trans conformation by the requirements of the ring.

13.26 Asetilenik bileşikler Diels–Alder tepkimesinde dienofil olarak kullanılabilirler (Problem 13.14'e bakınız). 1,3-Bütadienin aşağıdaki reaktifler ile tepkimesinden elde edilmesi beklenen ürünlerin yapılarını yazınız.

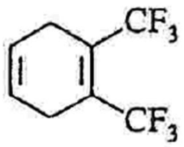
(a) 
$CH_3O\overset{O}{\overset{\|}{C}}C\equiv C\overset{O}{\overset{\|}{C}}OCH_3$ (dimetil asetilendikarboksilat)

(b) $CF_3C\equiv CCF_3$ (heksafloro-2-bütin)

13.26 (a)

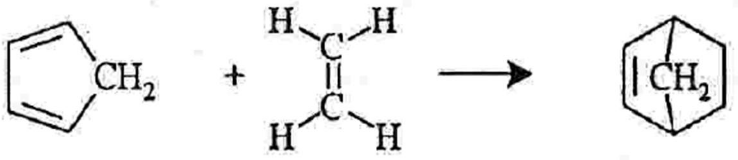


(b)

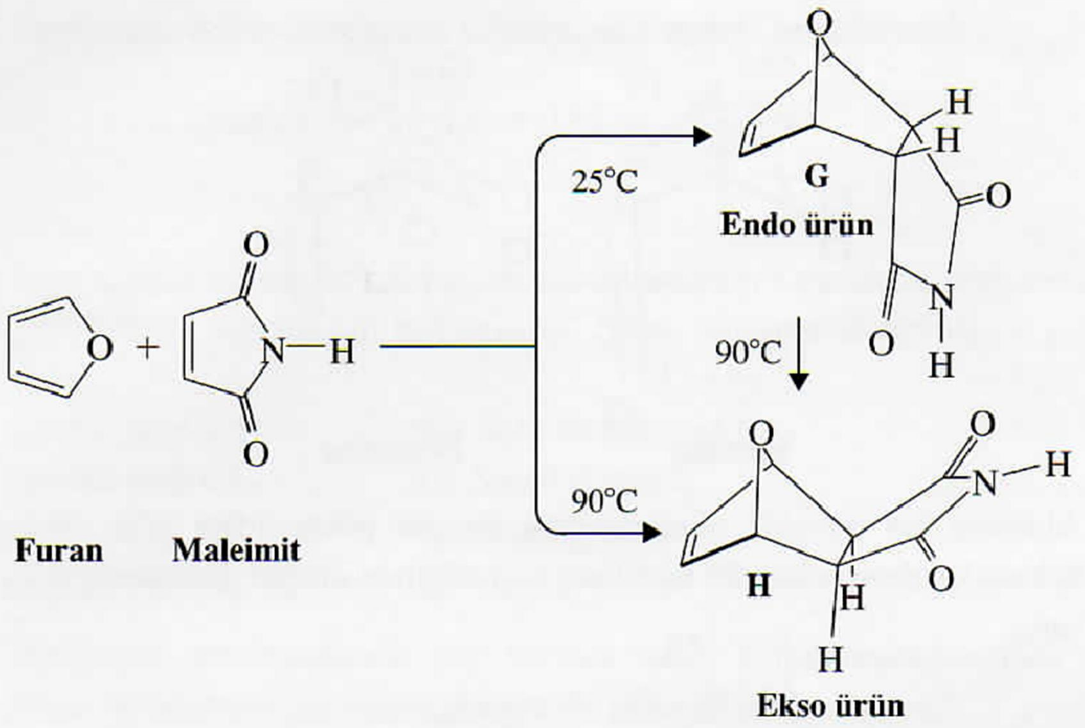


13.27 Siklopentadien eten ile 160–180°C'da bir Diels–Alder tepkimesi verir. Bu tepkime ürününün yapısını yazınız.

13.27

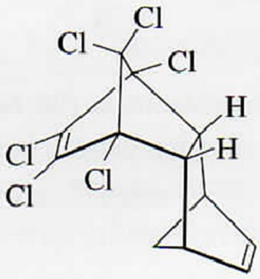


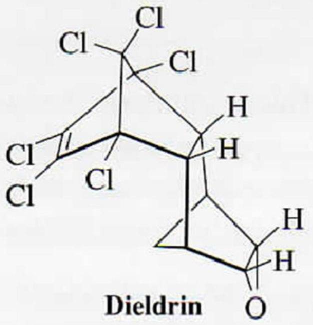
13.28 Furan ve maleimit 25°C'da Diels – Alder tepkimesi verdiğinde başlıca endo ürün **G** oluşur. Tepkimesi 90°C'da gerçekleştirildiği zaman, başlıca ürün izomer **H**'dir. Endo ürün 90°C'a ısıtıldığı zaman ekso ürüne izomerleşir. Bu sonuçlar için bir açıklama getiriniz.

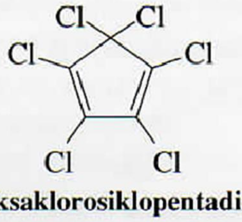


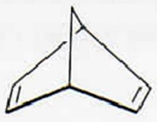
13.28 The endo adduct is less stable than the exo, but is produced at a faster rate at 25°C. At 90°C the Diels-Alder reaction becomes reversible; an equilibrium is established, and the more stable exo adduct predominates.

13.29 Aldrin ve dieldrin çok tartışılan iki "sert" böcek öldürücüdür (aşağıya bakınız). [Çevre Koruma Komitesi (EPA) bu böcek öldürücülerin kullanımını muhtemel yan etkileri ve biyolojik olarak ayrışamamaları nedeniyle durdurmuştur.] Aldrinin ticari sentezi norbornadien ve heksaklorosiklopentadien ile başlar. Dieldrin ise aldrinden sentezlenir. Bu sentezlerin nasıl yapılabileceğini gösteriniz.

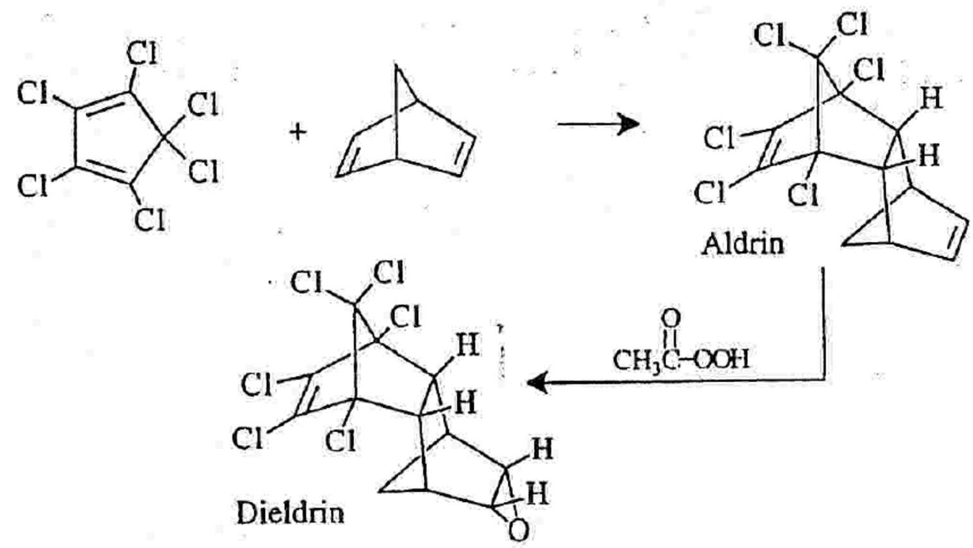

Aldrin


Dieldrin


Heksaklorosiklopentadien

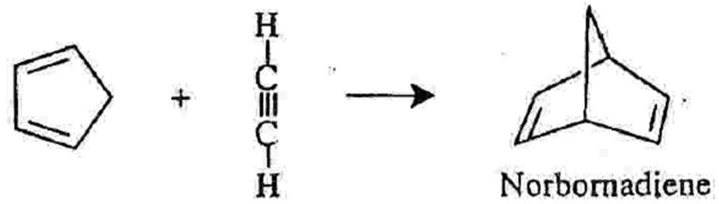

Norbornadien

13.29

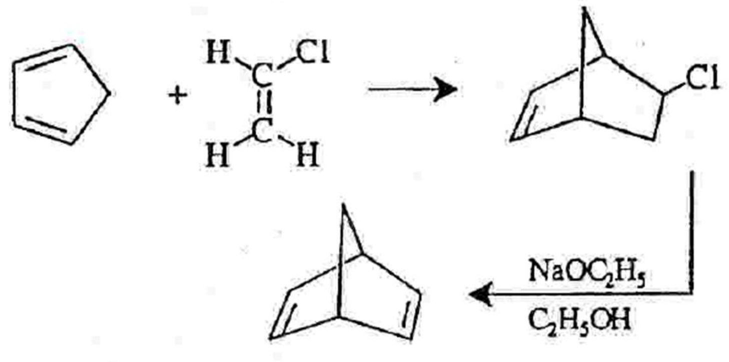


13.30 **(a)** Aldrinin sentezi için kullanılan norbornadien, asetilen ve siklopentadienden hazırlanabilir (Problem 13.29). İlgili tepkimeyi gösteriniz.
(b) Bu ürün, siklopentadienin vinil klorürle tepkimeye sokulup oluşan ürünün bir bazla etkileştirilmesiyle de elde edilebilir. Bu sentezi tasarlayınız.

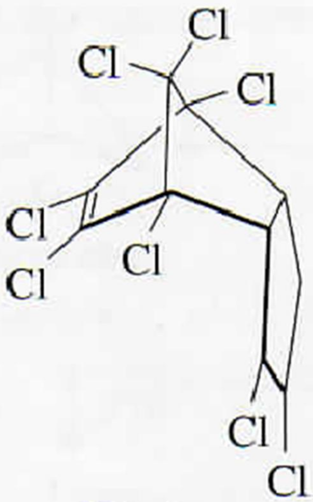
13.30 (a)



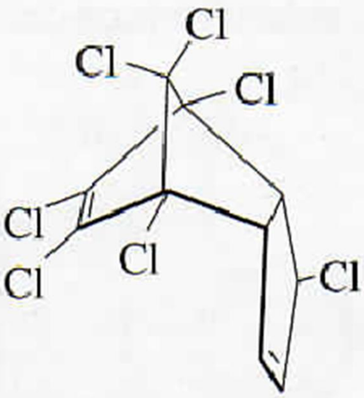
(b)



13.31 Diğer iki güçlü böcek öldürücü (Problem 13.29'a bakınız) klordan ve heptaklordur. Bunların ticari sentezi siklopentadien ve heksaklorosiklopenladien ile başlar. Bu sentezlerin nasıl yapılabileceğini gösteriniz.

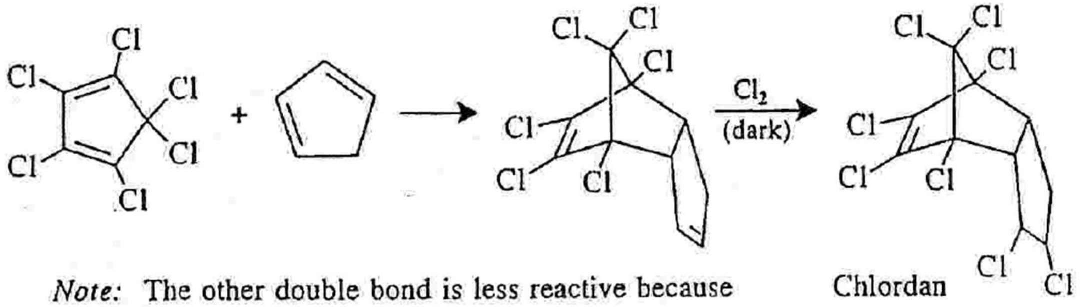


Klordan



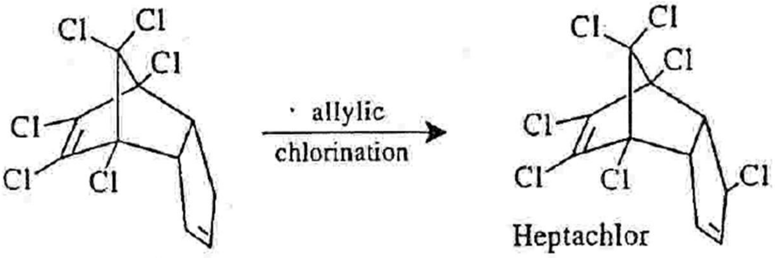
Heptaklor

13.31



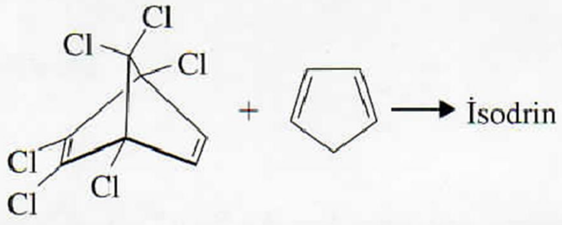
Chlordan

Note: The other double bond is less reactive because of the presence of the two chlorine substituents.

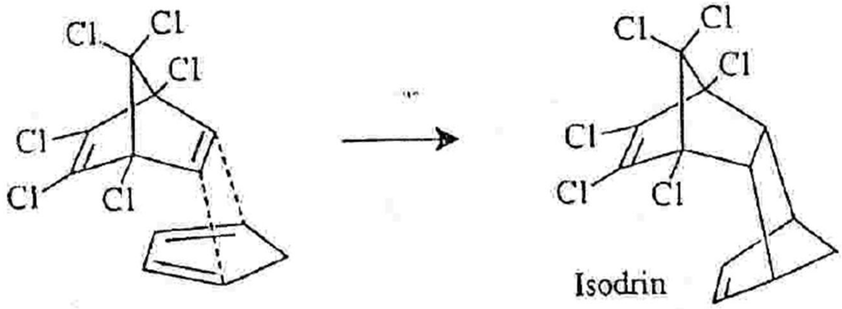


Heptachlor

13.32 Aldrinin bir izomeri olan isodrin, burada gösterildiği gibi, siklopentadien, heksaklorobornadien ile tepkimeye girdiğinde oluşur. İsodrin için bir yapı öneriniz.



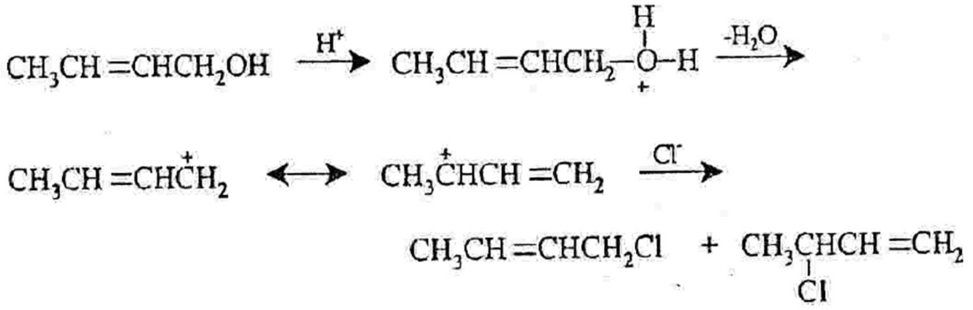
13.32



Isodrin

13.33 $CH_3CH{=}CHCH_2OH$ derişik HC1 ile etkileştirildiğinde iki ürün, $CH_3CH{=}CHCH_2C1$ ve $CH_3CHC1CH{=}CH_2$, oluşur. Bunu açıklayan bir mekanizma öneriniz.

13.33 Protonation of the alcohol and loss of water lead to an allylic cation that can react with a chloride ion at either C1 or C3.

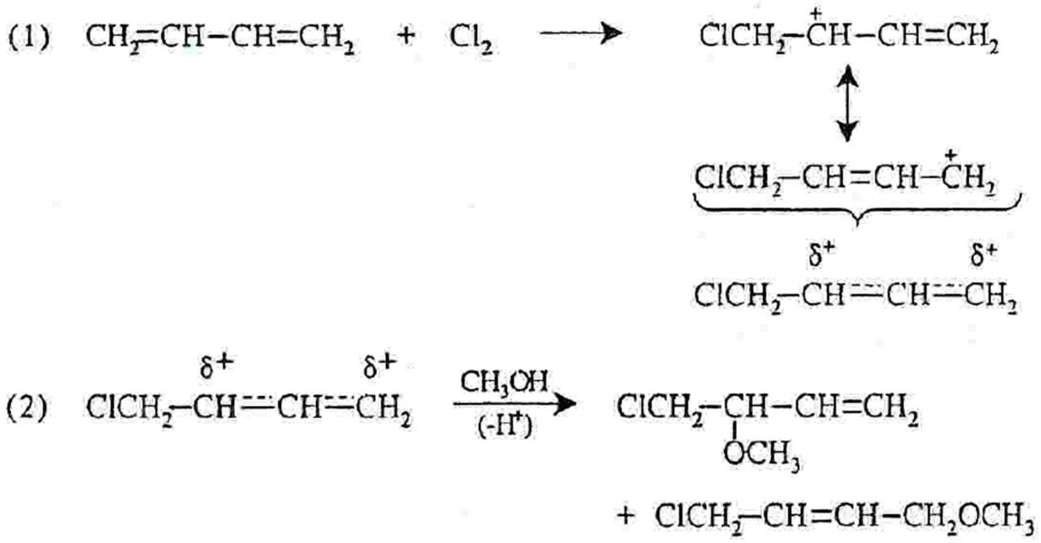


$$CH_3CH{=}CHCH_2OH \xrightarrow{H^+} CH_3CH{=}CHCH_2{-}\overset{H}{\underset{+}{O}}{-}H \xrightarrow{-H_2O}$$

$$CH_3CH{=}CH\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}HCH{=}CH_2 \xrightarrow{Cl^-} CH_3CH{=}CHCH_2Cl + CH_3\underset{Cl}{C}HCH{=}CH_2$$

13.34 1,3-Bütadienin CH_3OH'deki bir çözeltisi klor ile etkileştirildiğinde, ürünler $C1CH_2CH{=}CHCH_2OCH_3$ (%30) ve $C1CH_2\underset{OCH_3}{C}HCH{=}CH_2$ (%70) dir. Bunların oluşumunu gösteren bir mekanizma yazınız.

13.34

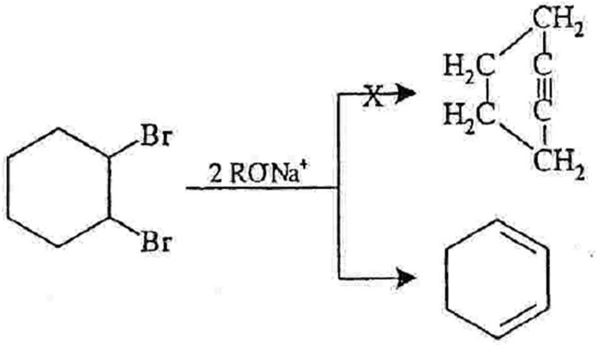


$$(1)\quad CH_2{=}CH{-}CH{=}CH_2 + Cl_2 \longrightarrow ClCH_2{-}\overset{+}{C}H{-}CH{=}CH_2 \;\updownarrow\; \underbrace{ClCH_2{-}CH{=}CH{-}\overset{+}{C}H_2}_{ClCH_2{-}\overset{\delta+}{CH}{\overset{\cdots}{=}}CH{\overset{\cdots}{=}}\overset{\delta+}{CH_2}}$$

$$(2)\quad ClCH_2{-}\overset{\delta+}{CH}{\overset{\cdots}{=}}CH{\overset{\cdots}{=}}\overset{\delta+}{CH_2} \xrightarrow[(-H^+)]{CH_3OH} ClCH_2{-}\underset{OCH_3}{C}H{-}CH{=}CH_2 + ClCH_2{-}CH{=}CH{-}CH_2OCH_3$$

13.35 *komşu*-Dihalojenürlerin dehidrohalojenlenmesi (iki eşdeğer mol HX'in çıkarılması) normal olarak bir konjuge dienden daha çok bir alkini verir. Halbuki, 1,2-dibromosikloheksan dehidrohalojenlendiğinde 1,3-sikloheksadien iyi bir verimle elde edilir. Bunu etkileyen etken nedir?

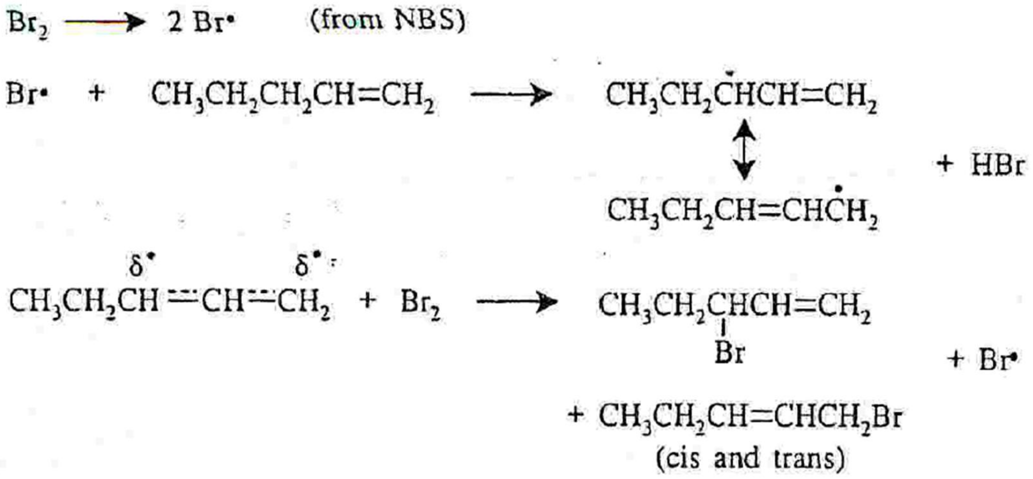
13.35 A six-membered ring cannot accommodate a triple bond because of the strain that would be introduced.



Too highly strained

13.36 1-Penten, *N*-bromosüksinimit ile tepkimeye girdiğinde, C_5H_9Br formüllü iki ürün elde edilir. Bu ürünler nelerdir ve nasıl oluşurlar?

13.36 The products are $CH_3CH_2\overset{Br}{\overset{|}{C}}HCH=CH_2$ and $CH_3CH_2CH=CHCH_2Br$ (cis and trans). They are formed from an allylic radical in the following way:



$$Br_2 \longrightarrow 2\,Br\cdot \quad \text{(from NBS)}$$

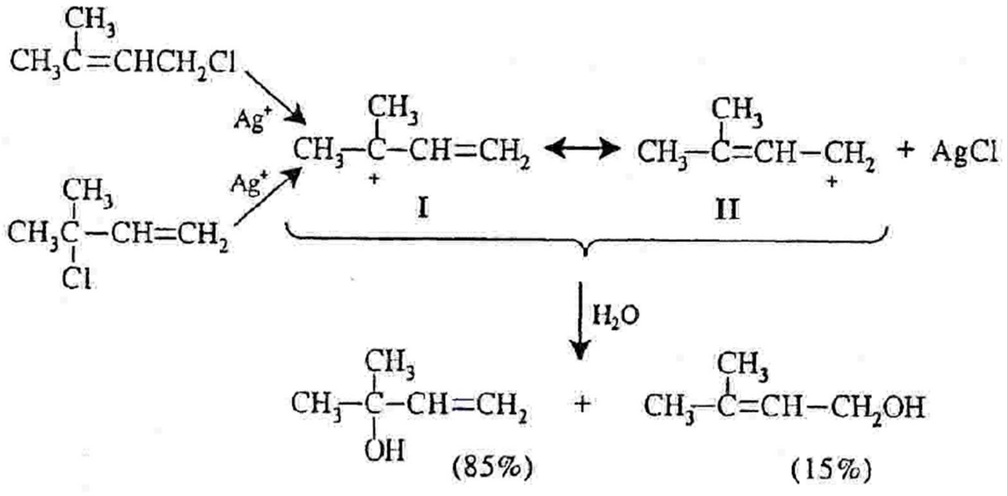
$$Br\cdot + CH_3CH_2CH_2CH=CH_2 \longrightarrow CH_3CH_2\dot{C}HCH=CH_2 \updownarrow CH_3CH_2CH=CH\dot{C}H_2 + HBr$$

$$CH_3CH_2\overset{\delta\cdot}{CH}\overset{--}{=}CH\overset{--}{=}\overset{\delta\cdot}{CH_2} + Br_2 \longrightarrow CH_3CH_2\underset{Br}{\underset{|}{C}}HCH=CH_2 + Br\cdot$$

$$+\ CH_3CH_2CH=CHCH_2Br \quad \text{(cis and trans)}$$

13.37 1-Kloro-3-metil-2-büten veya 3-kloro-3-metil-1-büten su içerisinde Ag_2O ile etkileştirildiğinde alkollerin aynı karışımını ($AgCl$'e ek olarak) verir: $(CH_3)_2C=CHCH_2OH$ (%15) ve $(CH_3)_2\underset{OH}{\underset{|}{C}}CH=CH_2$ (%85). **(a)** Bu ürünlerin oluşumunu gösteren bir mekanizma yazınız. **(b)** Oluşan iki alkenin bağıl oranları nasıl açıklanabilir?

13.37 (a) The same carbocation (a resonance hybrid) is produced in the dissociation step:



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2Cl \xrightarrow{Ag^+} \quad CH_3\underset{\quad CH_3\overset{CH_3}{\overset{|}{C}}-CH=CH_2}{} $$

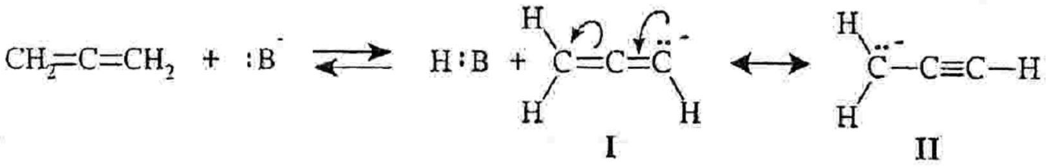
$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2Cl \text{ or } CH_3\overset{CH_3}{\overset{|}{C}}(Cl)-CH=CH_2 \xrightarrow{Ag^+} \underbrace{\underset{\textbf{I}}{CH_3-\overset{CH_3}{\overset{|}{\underset{+}{C}}}-CH=CH_2} \longleftrightarrow \underset{\textbf{II}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\underset{+}{CH_2}}} + AgCl$$

$$\xrightarrow{H_2O} \underset{(85\%)}{CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH=CH_2} + \underset{(15\%)}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2OH}$$

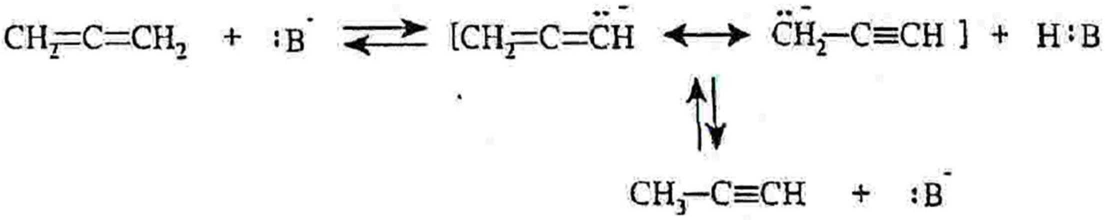
(b) Structure **I** contributes more than **II** to the resonance hybrid of the carbocation (rule 8). Therefore, the hybrid carbocation has a larger partial positive charge on the tertiary carbon atom than on the primary carbon atom. Reaction of the carbocation with water will therefore occur more frequently at the tertiary carbon atom.

13.38 Allenin hidrojenlenme ısısı 298 kJ mol^{-1}'dür, halbuki propininki 290 kJ mol^{-1}'dir. **(a)** Hangi bileşik daha kararlıdır? **(b)** Allen ile kuvvetli bir bazın etkileştirilmesi propine izomerleşmesine yol açar. Niçin? Açıklayınız.

13.38 (a) Propyne. (b) Base (: B^-) removes a proton, leaving the anion whose resonance structures are shown:



Reaction with H:B may then occur at the CH_2 carbanion. The overall reaction is



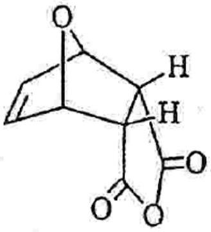
$$\mathrm{CH_2{=}C{=}CH_2} \; + \; :\mathrm{B}^- \rightleftharpoons [\mathrm{CH_2{=}C{=}\overset{..\,-}{C}H} \longleftrightarrow \mathrm{\overset{..\,-}{C}H_2{-}C{\equiv}CH}] \; + \; \mathrm{H{:}B}$$

$$\updownarrow$$

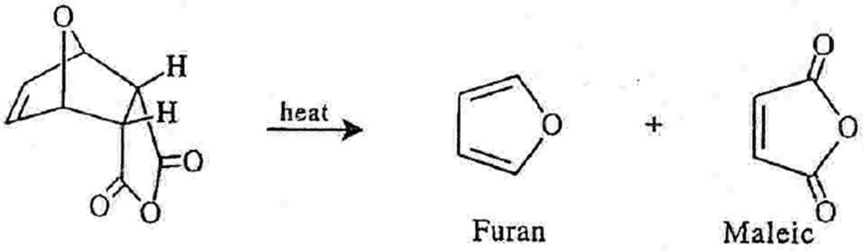
$$\mathrm{CH_3{-}C{\equiv}CH} \; + \; :\mathrm{B}^-$$

13.39 Dietil eter içerisindeki maleik anhidrit ile furanın (Problem 13.28) karıştırılması erime noktası 125°C olan katı bir kristal verir. Bu bileşik eridiği zaman bir gaz çıkışı olduğunu görürsünüz. Eğer erimiş madde tekrar katılaşmaya bırakılırsa, erime noktası artık 125°C yerine 56°C bulunur. Uygun bir kimya el kitabına bakarak, neler olduğunu açıklayan bir açıklama öneriniz.

13.39 The first crystalline solid is the Diels-Alder adduct below, mp 125°C,



On melting, this adduct undergoes a reverse Diels-Alder reaction, yielding furan (which vaporizes) and maleic anhydride, mp 56°C,



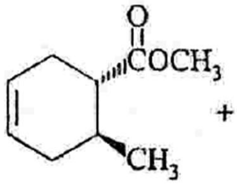
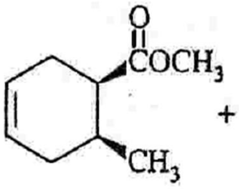
13.40 1,3-Bütadien aşağıdakilerin her biri ile tepkime verdiğinde oluşabilecek ürünlerin yapılarını yazınız.

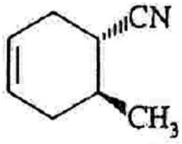
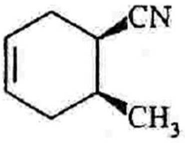
(a) (*E*)-$CH_3CH{=}CHCO_2CH_3$

(b) (*Z*)-$CH_3CH{=}CHCO_2CH_3$

(c) (*E*)-$CH_3CH{=}CHCN$

(d) (*Z*)-$CH_3CH{=}CHCN$

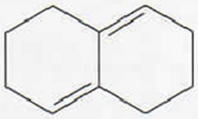
13.40 (a)  + enantiomer (b)  + enantiomer

(c)  + enantiomer (d)  + enantiomer

13.41 Bütil bromür ve 4-bromo-1-bütenin her ikisi de birincil halojenürler olduğu halde, ikincisi daha hızlı ayrılma verir. Bu davranış asıl açıklanabilir?

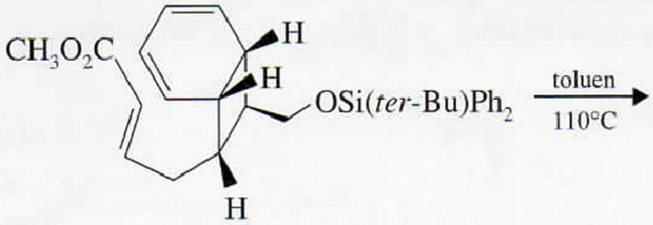
13.41 The product formed when butyl bromide undergoes elimination is 1-butene, a simple monosubstituted alkene. When 4-bromo-1-butene undergoes elimination, the product is 1,3-butadiene, a conjugated diene, and therefore, a more stable product. The transition states leading to the products reflect the relative stabilities of the products. Since the transition state leading to 1,3-butadiene has the lower free energy of activation of the two, the elimination reaction of 4-bromo-1-butene will occur more rapidly.

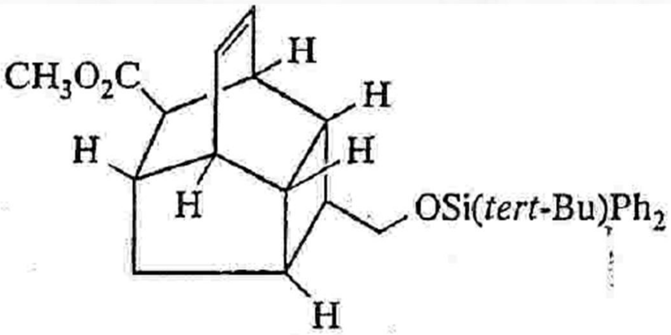
13.42 Aşağıda gösterilen molekül bir konjuge dien olmasına rağmen, niçin bir Diels – Alder tepkimesi vermez?



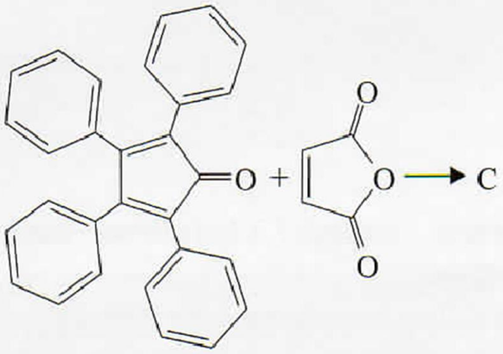
13.42 The diene portion of the molecule is locked into an s-trans conformation. It cannot, therefore, achieve the s-cis conformation necessary for a Diels-Alder reaction.

13.43 Aşağıdaki tepkimede oluşan ürünün yapısını çiziniz (K. C. Nicolaou tarafından endiandrik asitlerden birinin sentezi esnasında oluştu).



13.43 

***13.44** Tetrafenilsiklopentadienon (**A**) maleik anhidrit (**B**) ile ısıtıldığında, **A**' nın koyu eflatun rengi kaybolur, karbon monoksit çıkar ve son ürün olarak **C** oluşur. Tepkime bir Diels – Alder ara ürünü üzerinden yürür. **C** bileşiği δ 3,7; 7,1; 7,3 ve 7,4'de birli ¹H NMR piklerine sahiptir (alan oranları 1 : 2 : 4 : 4).

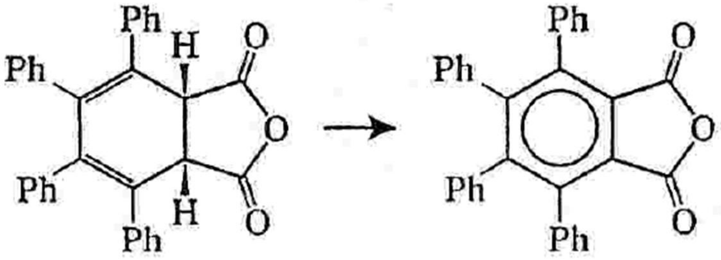


A **B**

C bir eşdeğer mol bromürle tepkimeye girerse, iki hidrojen atomunun yükseltgenme sonucu çıkmasıyla iki eşdeğer mol HBr oluşur. Meydana gelen ürün **D**'dir. **D** sadece δ 7,2; 7,3, ve 7,5'de ¹H NMR pikleri verir (alan oranları 1 : 2 : 2).

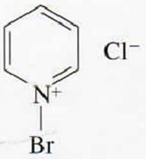
C ve **D**'nin yapıları nasıldır?

***13.44**



C **D**

***13.45** (**a**) Siklopentadienle ilgili bir çalışmada siklopentadien ile BrCl (piridinin katılma ürünü şeklinde 1, *N*–bromopiridinyum klorür olarak tepkimeye sokulduğunda baskın olarak BrCl'nin 1,2-katılma ürünü oluştu. Katılma markovnikov katılmasıdır ve basit alkenlere bromür katılmasının stereokimyasına benzer. Ürünün yapısını çiziniz. (**b**) BrCl'nin kendini serbest olarak kendi kendine kullanıldığı zaman (yani pridin katılma kompleksi olarak değil) *cis*-1,4-katılması baskındır. Bu ürünün yapısını çiziniz. (**c**) Yukarıdaki iki katılma ürününün metilen grupları ¹H NMR spektrumları ile ayırdedilebilir ki bunlar:

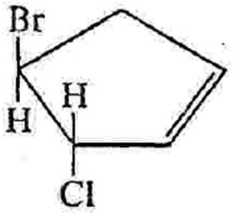


N-Bromopiridinyium klorür

İzomer **1** için:
CH_2'nin H_a'sı: δ 2,57 (çift üçlü, J değerleri 2,5 ve 16 Hz)
CH_2'nin H_b'si: δ 3,14 (çift üçlü, J değerleri 6,6 ve 16 Hz)

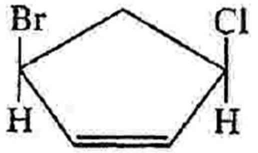
İzomer **2** için:
CH_2'nin H_a'sı: δ 2,76 (geniş ikili, J değeri 18 Hz)
CH_2'nin H_b'si: δ 3,35 (çift ikili, J değerleri 5,5 ve 18 Hz)
Hangi izomer hangisidir?

*13.45 (a)



(isomer *2*)

(b)



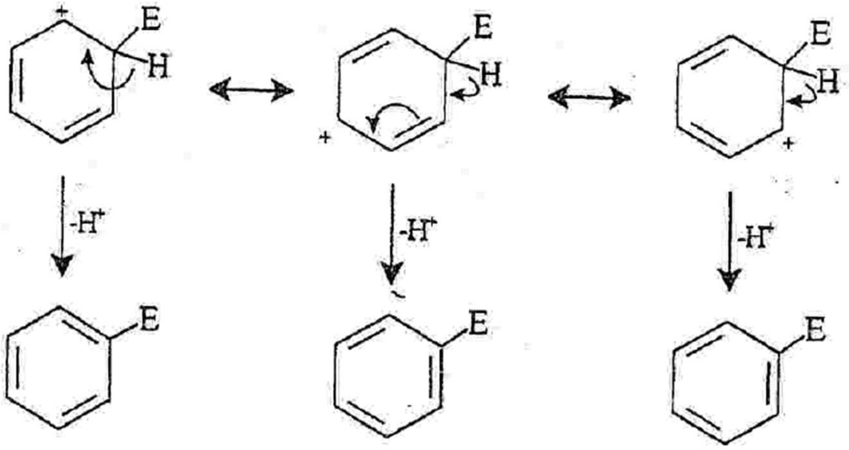
(isomer *1*)

(c) See above

Aromatik Bileşiklerin Tepkimeleri

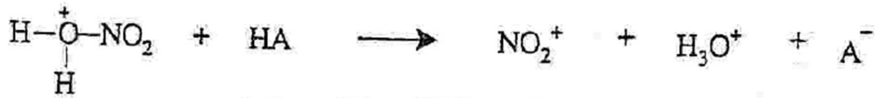
Problem 15.1 ➤ Arenyum iyonu için olan üç rezonans yapıdan her birisini kullanarak bir proton çıkışının nasıl olduğunu ve her bir gösterilişin üç konjuge ikili bağa sahip (yani, altı tam delokalize olmuş π elektronu olan) benzen halkasını nasıl oluşturduğunu gösteriniz.

15.1



Problem 15.2 ➤ H_2SO_4'ün pK_a değeri – 9, HNO_3'ün pK_a değeri –1,4'tür. Nitrolamanın neden derişik nitrik ve sülfürik asit karışımında, sadece derişik nitrik asitle yapılana göre daha hızlı gerçekleştiğini açıklayınız.

15.2 The rate is dependent on the concentration of NO_2^+ ion formed from protonated nitric acid.

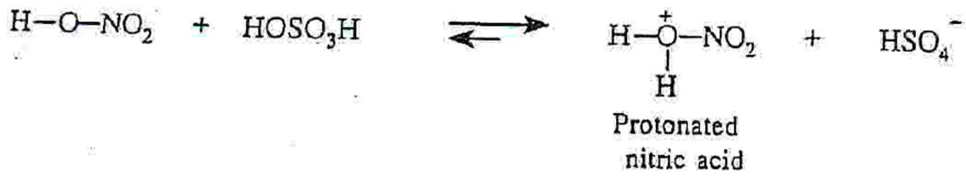


$$H-\overset{+}{\underset{|}{O}}(H)-NO_2 + HA \longrightarrow NO_2^+ + H_3O^+ + A^-$$

(where HA = HNO_3 or $HOSO_3H$)

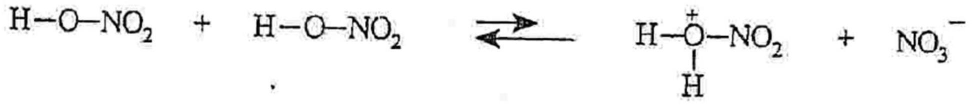
Because H_2SO_4 ($HOSO_3H$) is a stronger acid, a mixture of it and HNO_3 will contain a higher concentration of protonated nitric acid than will nitric acid alone.

That is, the reaction,



$$H-O-NO_2 + HOSO_3H \rightleftharpoons H-\overset{+}{\underset{|}{O}}(H)-NO_2 + HSO_4^-$$

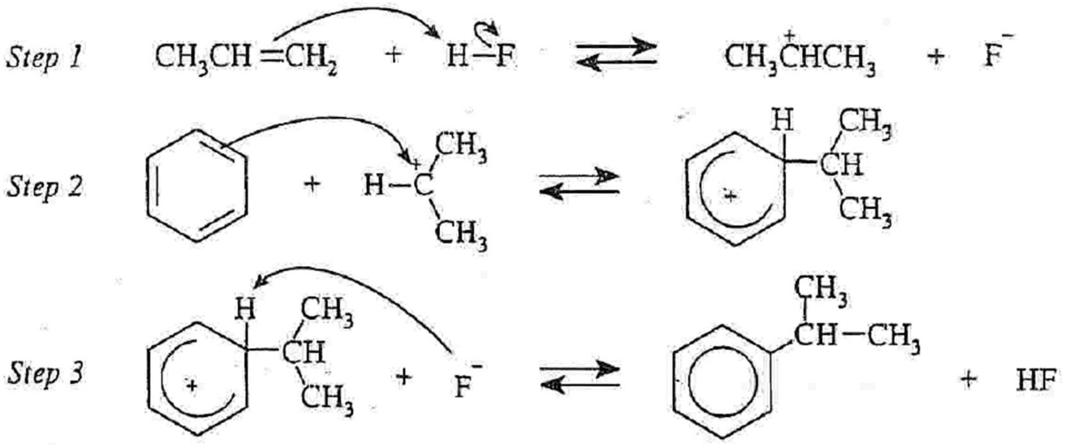
produces more protonated nitric acid than the reaction,



$$H-O-NO_2 + H-O-NO_2 \rightleftharpoons H-\overset{+}{\underset{|}{O}}(H)-NO_2 + NO_3^-$$

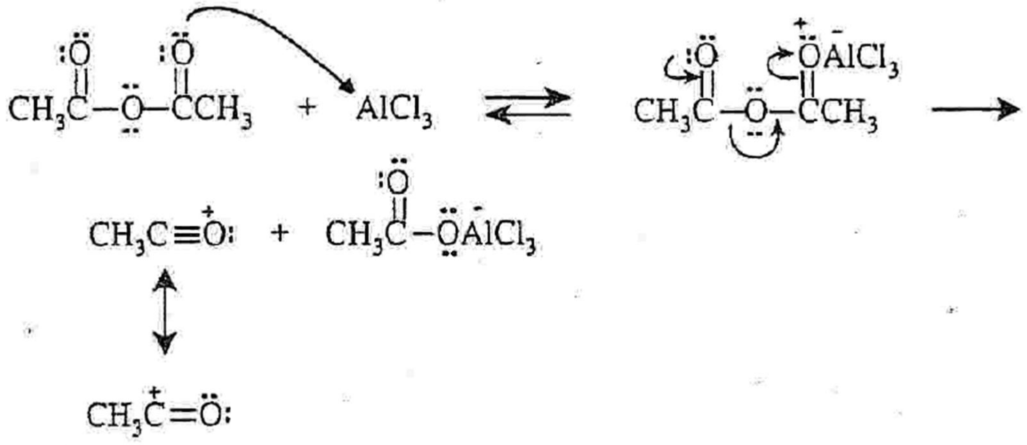
Sıvı HF içerisindeki benzen ve propenden (yukarıda gösterilen) izopropil benzen oluşumunu gösteren tepkime için mantığa uygun tüm basamakları içeren bir mekanizma yazınız. Mekanizmanız ürünün niçin propilbenzen olmayıp izopropilbenzen olduğunu açıklamalıdır. ◄ **Problem 15.3**

15.3



$AlCl_3$ varlığında, Asetik anhidritten, açilyum iyonunun nasıl oluştuğunu gösteriniz. ◄ **Problem 15.4**

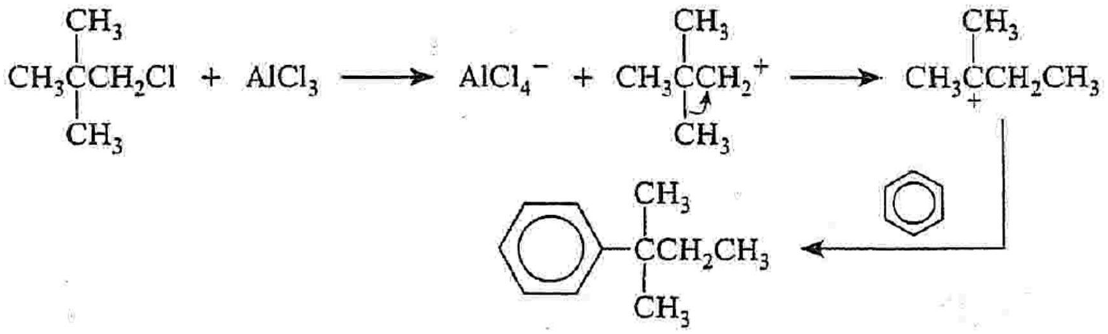
15.4



Problem 15.5

Benzen, alüminyum klorürlü ortamda neopentil klorür ile tepkimeye girdiğinde ana ürün neopentilbenzen değil, 2-metil-2-fenilbütandır. Bu sonucu açıklayınız.

15.5 The carbocation formed by the action of $AlCl_3$ on neopentyl chloride is primary. This carbocation rearranges to the more stable tertiary carbocation before it can react with the benzene ring:



Problem 15.6

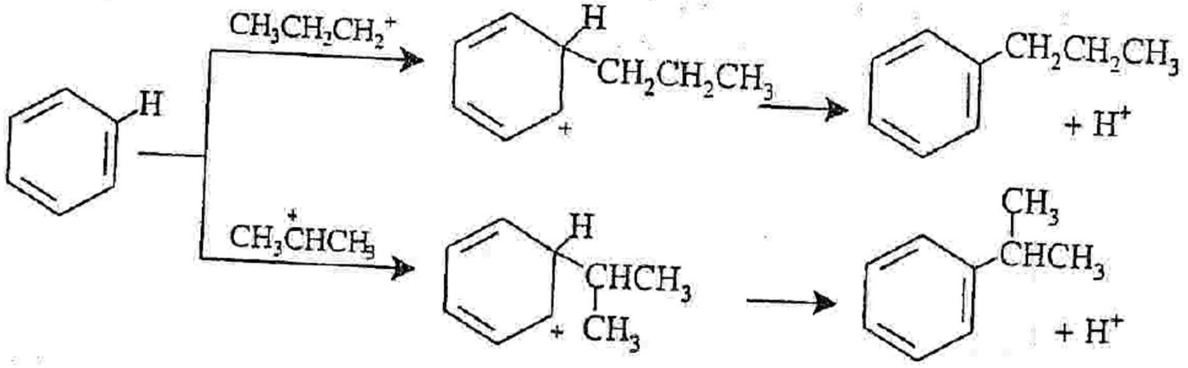
Benzen bor triflorürlü ortamda propil alkolle tepkimeye girdiğinde ürün olarak propilbenzen ve izopropilbenzen elde edilmiştir. Bu sonucu gösteren bir mekanizma yazınız.

15.6 $CH_3CH_2CH_2{-}OH + BF_3 \rightleftharpoons CH_3CH_2CH_2^+ + HOBF_3$

The propyl cation can rearrange into an isopropyl cation:

$$CH_3CH_2CH_2^+ \xrightarrow[\text{shift}]{\text{hydride}} CH_3\overset{+}{C}HCH_3$$

Both carbocations can then attack the ring.



Problem 15.7

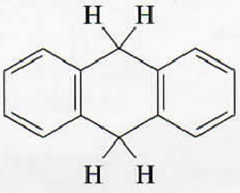
Benzen ve uygun açil klorür veya asit anhidritten başlayarak aşağıdakilerin her birinin sentezini özetleyiniz.

(a) Bütilbenzen

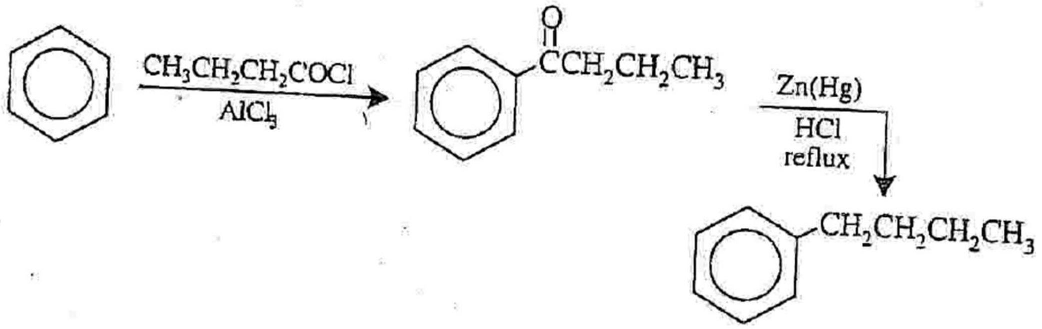
(b) $(CH_3)_2\ CHCH_2CH_2C_6H_5$

(c) Benzofenan ($C_6H_5COC_6H_5$)

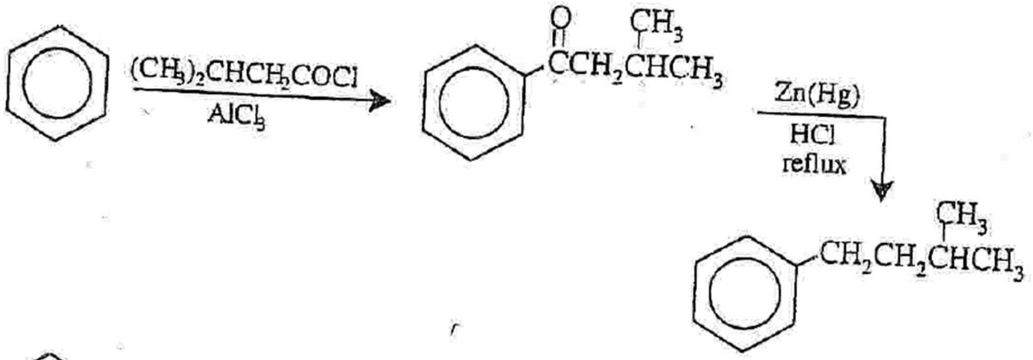
(d) 9.10-Dihidroantrosen


9,10-Dihidroanthrasen

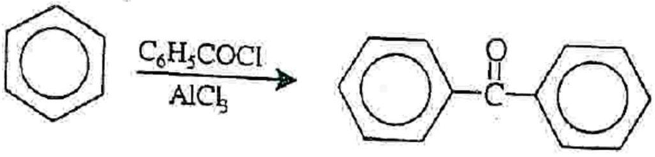
15.7 (a)



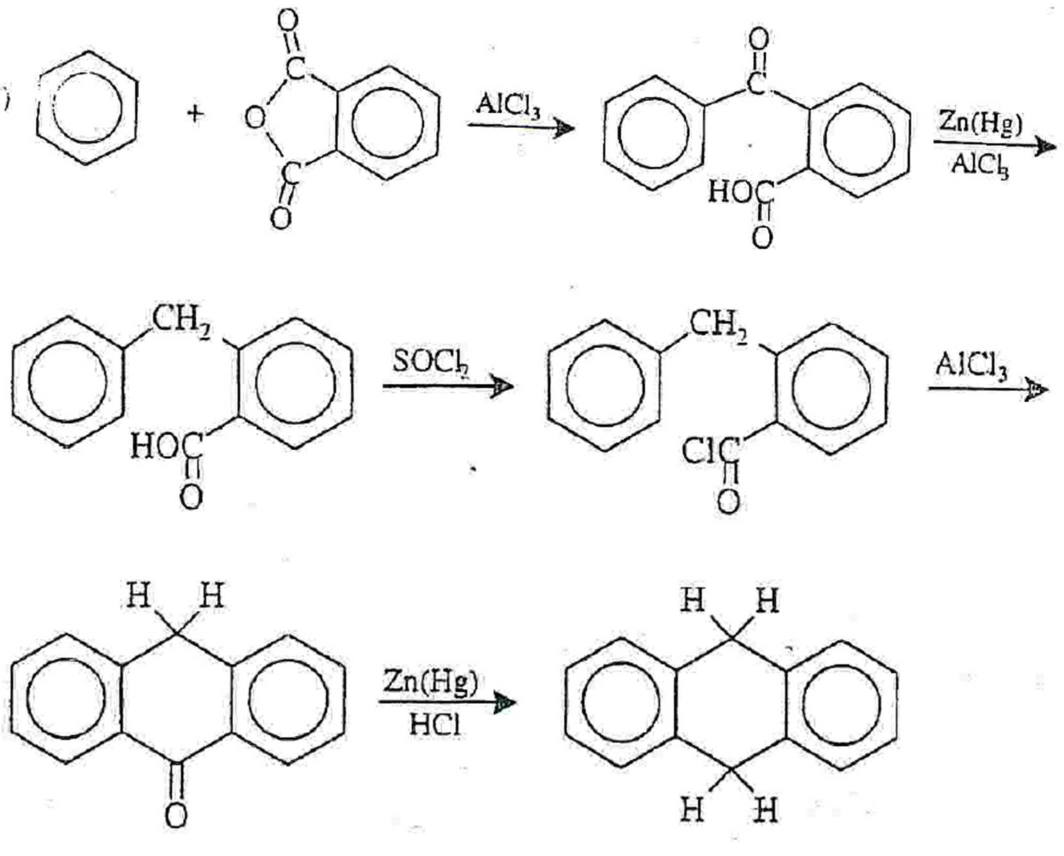
(b)



(c)



(d)



Problem 15.8 ➤ Metil grubunun gelen elektrofile hiç bir etkisinin olmadığını varsaydığınızda yukarıda verilen bileşiklerin oluşma yüzdeleri nasıl olurdu? Açıklayınız.

15.8 If the methyl group had no directive effect on the incoming electrophile, we would expect to obtain the products in purely statistical amounts. Since there are two ortho hydrogen atoms, two meta hydrogen atoms, and one para hydrogen, we would expect to get 40% ortho (2/5), 40% meta (2/5), and 20% para (1/5). Thus, we would expect that only 60% of the mixture of mononitrotoluenes would have the nitro group in the ortho or para position. And we would expect to obtain 40% of *m*-nitrotoluene. In actuality, we get 96% of combined *o*- and *p*-nitrotoluene and only 4% *m*-nitrotoluene. This shows the ortho-para directive effect of the methyl group.

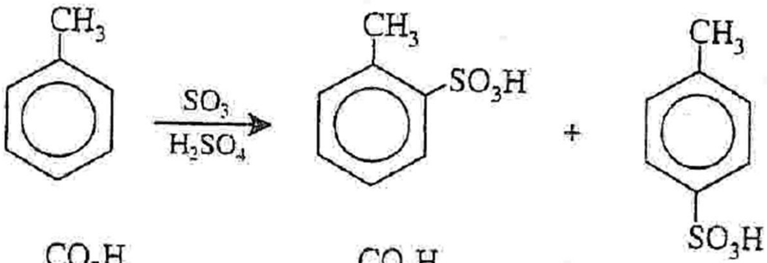
Problem 15.9

Aşağıdaki tepkimelerdeki ana ürünleri Çizelge 15.2'den yararlanarak yazınız.

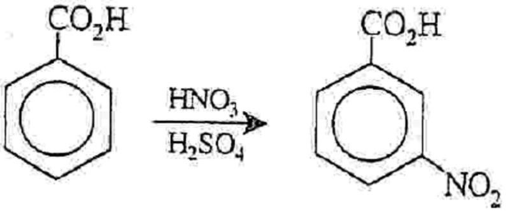
(a) Toluen sülfolanıyor.
(b) Benzoik asit nitrolanıyor.
(c) Nitrobenzen bromlanıyor.
(d) Fenol Friedel–Crafts tepkimesiyle açilleniyor.

Eğer ana ürünler orto ve para izomerlerinin bir karışımı oluyorsa onu da belirtiniz.

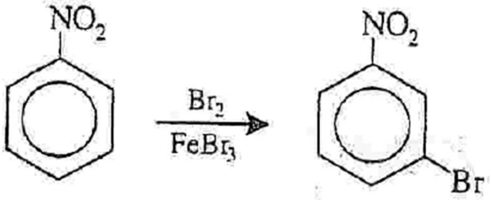
15.9 (a)



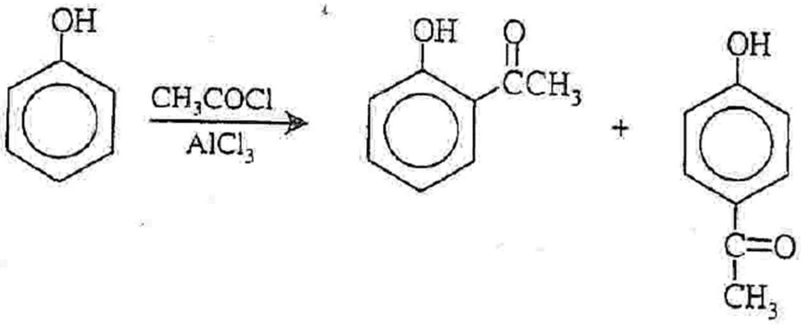
(b)



(c)



(d)

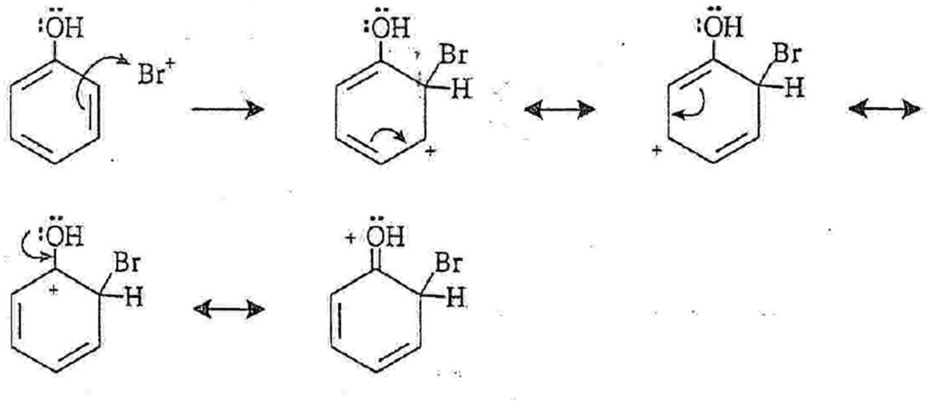


Problem 15.10

Rezonans teorisini kullanarak fenoldeki hidroksil grubunun niçin etkinleştirici ve orto–para yönlendirici bir grup olduğunu açıklayınız. Açıklamanızı, fenol, Br^+ ile orto, meta ve para konumlarında tepkimeye girdiğinde oluşan arenyum iyonlarını göstererek örneklendiriniz.

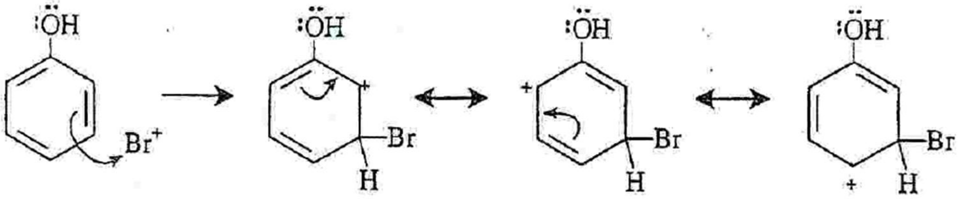
15.10 As the following structures show, attack at the ortho and para positions of phenol leads to arenium ions that are more stable (than the one resulting from meta attack) because they are hybrids of four resonance structures, one of which is relatively stable. Only three resonance structures are possible for the meta arenium ion, and none is relatively stable.

Ortho attack

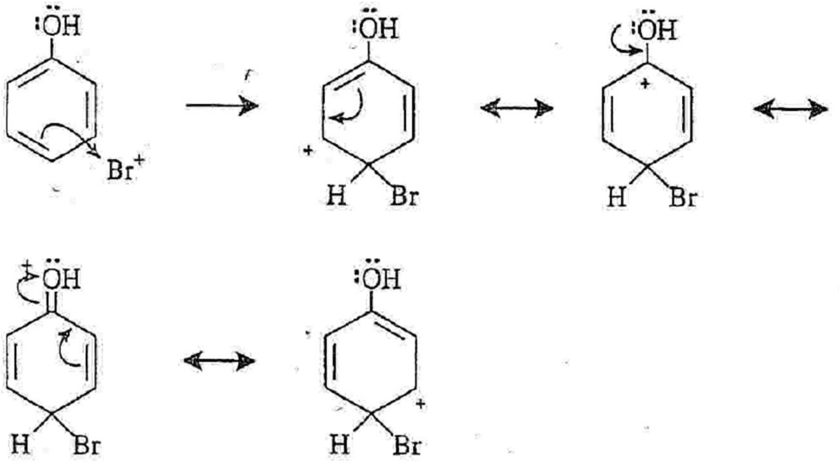


Relatively stable

Meta attack



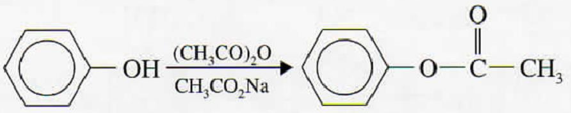
Para attack



Relatively stable

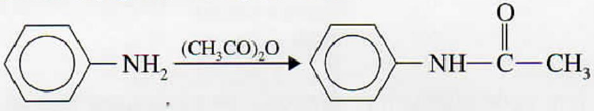
Problem 15.11

Fenol, sodyum asetat varlığında, asetik anhidritle tepkimeye girerek bir ester, fenil asetat, verir.



Fenol **Fenil asetat**

Fenil asetatın CH_3COO— grubu, fenoldeki —OH grubu gibi (Problem 15.10) orto–para yönlendiricidir. (a) CH_3COO— grubunun hangi yapısal özelliği bu durumu açıklar? (b) Fenil asetat *o* ve *p* konumlarından tepkimeye girmesine karşın elektrofilik aromatik yer değiştirmeye karşı fenolden daha az etkindir. Bunun sebebini açıklamak için rezonans teorisini kullanınız. (c) Anilin çoğu zaman elektrofilik aromatik yer değiştirme tepkimesinde çok etkindir ve istenmeyen tepkimeler de oluşur (Altbölüm 15.14A). Bu istenmeyen tepkimeleri önlemenin bir yolu; anilini, asetil klorür veya asetik anhidrit ile etkileştirerek asetanilite (aşağıda) dönüştürmektir.

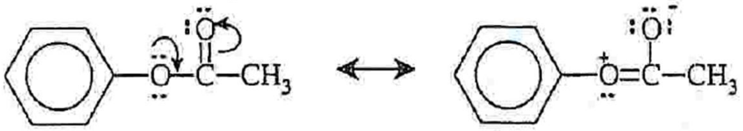


Anilin **Asetanilit**

Asetamido grubunun (CH_3CONH—) ne tür bir yönlendirici etkiye sahip olmasını beklersiniz? (d) Asetamido grubunun neden amino grubundan (—NH_2) daha az etkileştirici olduğunu açıklayınız.

15.11 (a) The atom (an oxygen atom) attached to the benzene ring has an unshared electron pair that it can donate to the arenium ions formed from ortho and para attack stabilizing them. (The arenium ions are analogous to the previous answer with a $-COCH_3$ group replacing the –H).

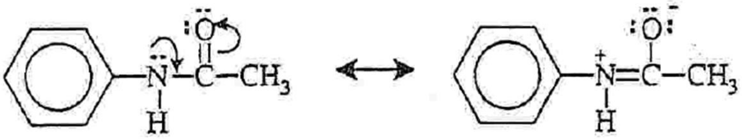
(b) Structures such as the following compete with the benzene ring for the oxygen electrons, making them less available to the benzene ring.



This effect makes the benzene ring of phenyl acetate less electron rich and, therefore, less reactive.

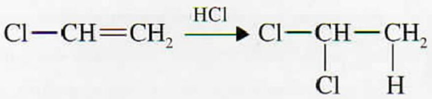
(c) Because the acetamido group has an unshared electron pair on the nitrogen atom that it can donate to the benzene ring it is an ortho-para director.

(d) Structures such as the following compete with the benzene ring for the nitrogen electrons, making them less available to the benzene ring.



Problem 15.12

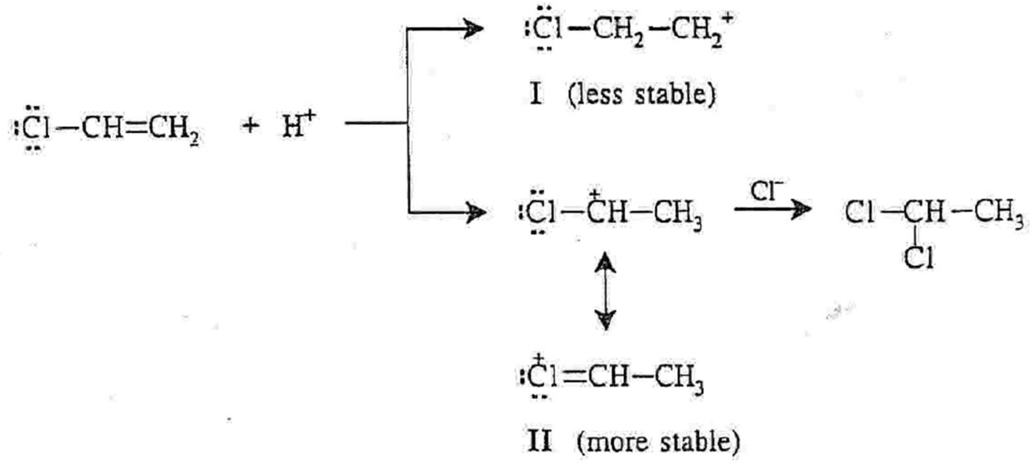
Hidrojen klorür kloroetene, etene katıldığından daha yavaş katılır ve ürün, 1,1-dikloroetandır. Rezonans ve indüktif etkileri kullanarak bu sonucu nasıl açıklarsınız?



$$Cl{-}CH{=}CH_2 \xrightarrow{HCl} Cl{-}\underset{\displaystyle Cl}{\underset{|}{C}H}{-}\underset{\displaystyle H}{\underset{|}{C}H_2}$$

15.12 The electron-withdrawing inductive effect of the chlorine of chloroethene makes its double bond less electron rich than that of ethene. This causes the rate of reaction of chloroethene with an electrophile (i.e., a proton) to be slower than the corresponding reaction of ethene.

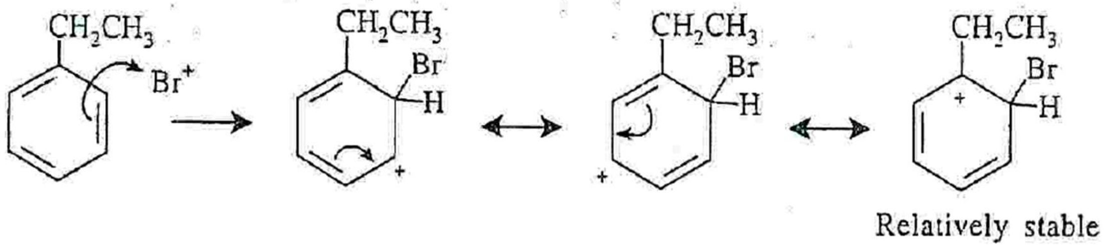
When chloroethene adds a proton, the orientation is governed by a resonance effect. In theory, two carbocations can form:



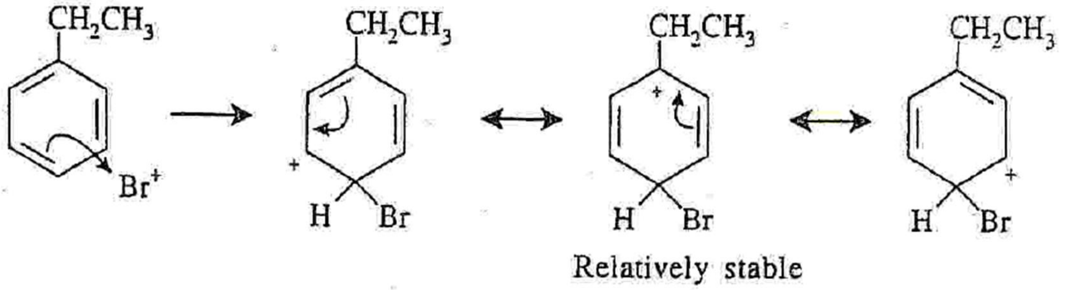
Carbocation II is more stable than I because of the resonance contribution of the extra structure just shown in which the chlorine atom donates an electron pair (see Section 15.11D).

Etilbenzen, Br$^+$ iyonu (Br_2 / $FeBr_3$'ten oluşur) ile tepkimeye girdiğinde oluşan orto ve para arenyum iyonları için rezonans yapılarını yazınız. ◂ **Problem 15.13**

15.13 ***Ortho attack***



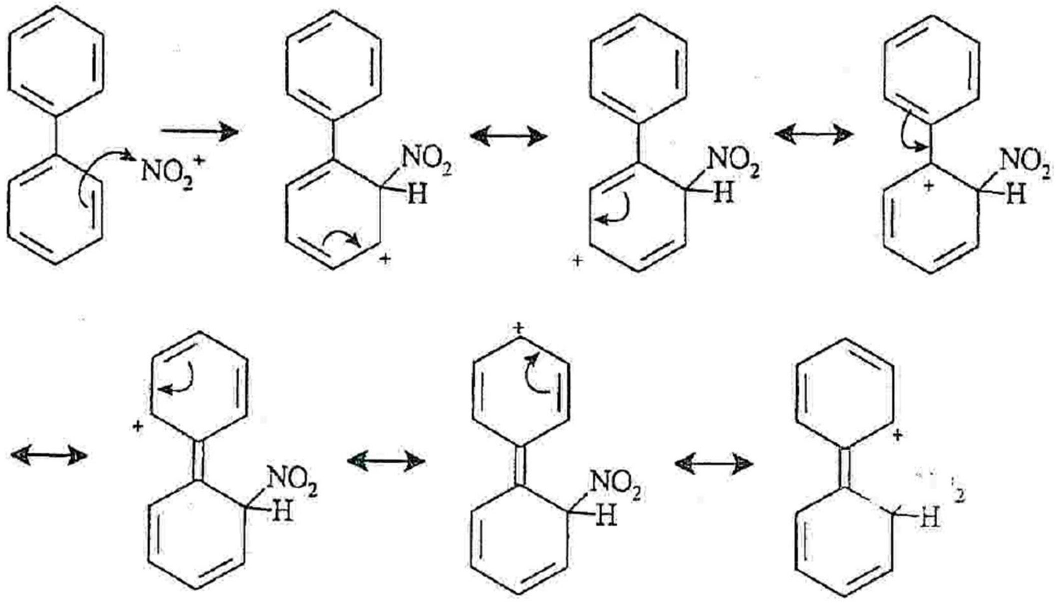
Para attack



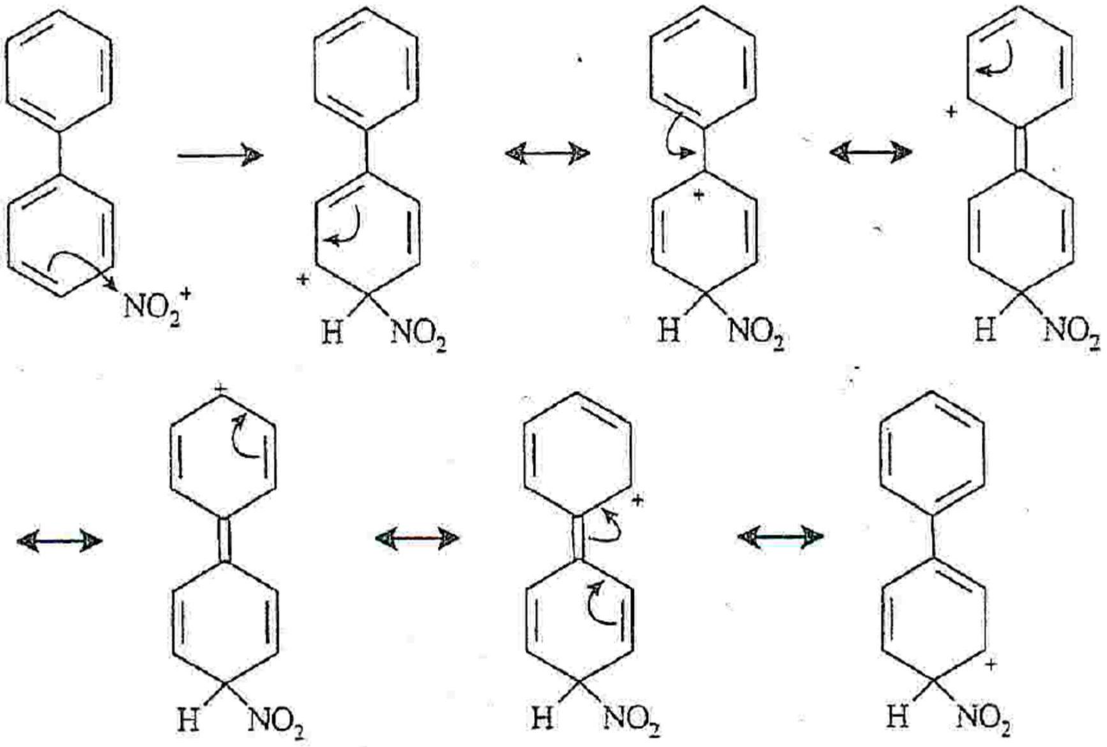
Bifenil (C_6H_5 — C_6H_5) nitrolandığında benzenden daha hızlı tepkimeye girer ve ana ürünler 1-nitro-2-fenilbenzen ve 1-nitro-4-fenilbenzendir. Bu sonuçları açıklayınız. ◂ **Problem 15.14**

15.14 The phenyl group, as the following resonance structures show, can act as an electron-releasing group and can stabilize the arenium ions formed from ortho and para attack.

Ortho attack



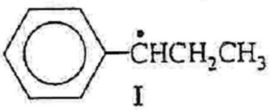
Para attack



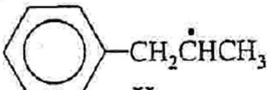
Problem 15.15

Propilbenzen UV ışını varlığında klor ile tepkimeye girdiğinde, ana ürün 1-kloro-1-fenilpropandır. 2-Kloro-1-fenilpropan ve 3-kloro-1-fenilpropan yan ürünlerdir. Her bir ürünü veren radikalin yapısını yazınız ve 1-kloro-1-fenilpropanın ana ürün olma nedenini açıklayınız.

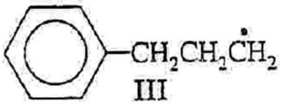
15.15



I leads to 1-chloro-1-phenylpropane

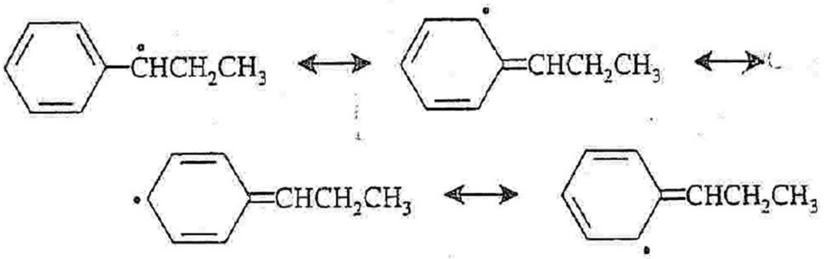


II leads to 2-chloro-1-phenylpropane



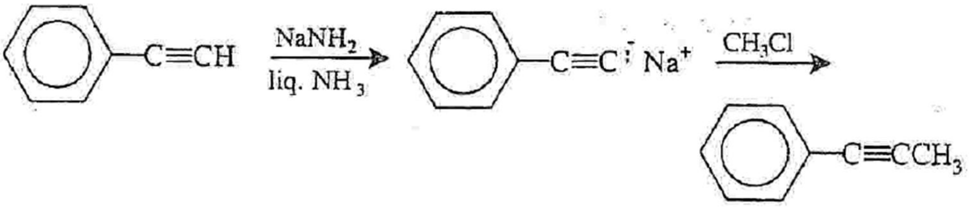
III leads to 1-chloro-3-phenylpropane

The major product is 1-chloro-1-phenylpropane because I is the most stable radical. It is a benzylic radical and therefore is stabilized by resonance.

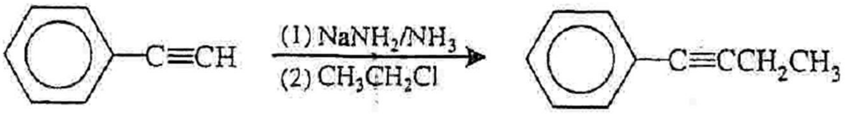


Problem 15.16 ➤ Fenilasetilen ($C_6H_5C{\equiv}CH$) ile başlayarak (a) 1-fenilpropin, (b) 1-fenil-1-bütin, (c) (*Z*)-1-fenilpropen ve (d) (*E*)-1-fenilpropenin sentezlerini tasarlayınız.

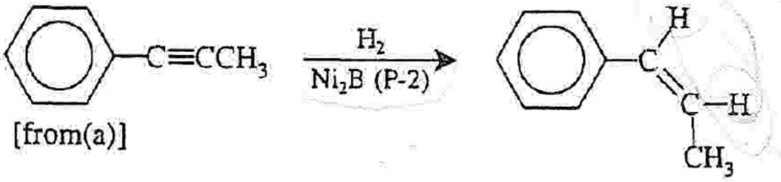
15.16 (a)



(b)

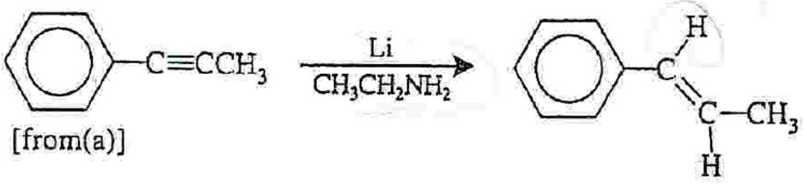


(c)



[from(a)]

(d)



[from(a)]

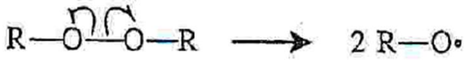
HBr'nin 1-fenilpropen ile (a) peroksit varlığındaki, (b) peroksitsiz ortamdaki tepkimeleri için mekanizmalar yazınız. Her bir durumda katılmanın yer seçiciliğinin sebebini açıklayınız (yani, peroksit varken 2-bromo-1-fenilpropanın peroksit yokken 1-bromo-1-fenilpropanın ana ürün olmasının nedenini açıklayınız). ◄ **Problem 15.17**

15.17 The addition of hydrogen bromide to 1-phenylpropene proceeds through a benzylic radical in the presence of peroxides, and through a benzylic cation in their absence (cf., a and b as follows).

(a) Hydrogen bromide addition in the presence of peroxides.

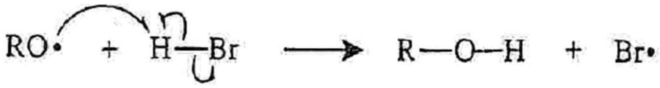
Chain Initiation

Step 1



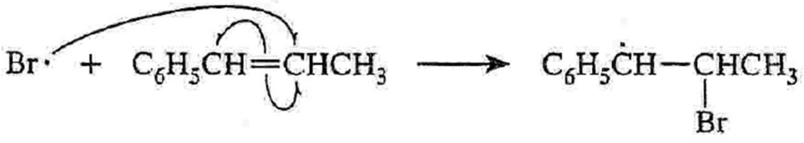
$$R{-}O{-}O{-}R \longrightarrow 2\,R{-}O\cdot$$

Step 2



$$RO\cdot + H{-}Br \longrightarrow R{-}O{-}H + Br\cdot$$

Step 3

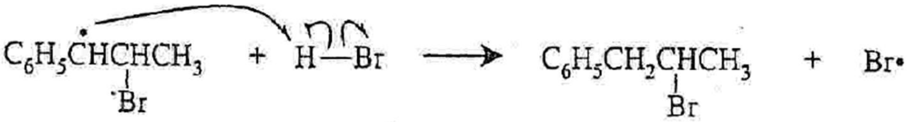


$$Br\cdot + C_6H_5CH{=}CHCH_3 \longrightarrow C_6H_5\dot{C}H{-}\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$

A benzylic radical

Chain Propagation

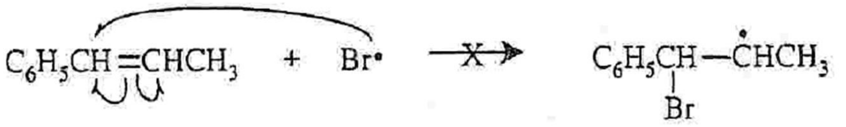
Step 4



$$C_6H_5\dot{C}H\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 + H{-}Br \longrightarrow C_6H_5CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 + Br\cdot$$

2-Bromo-1-phenylpropane

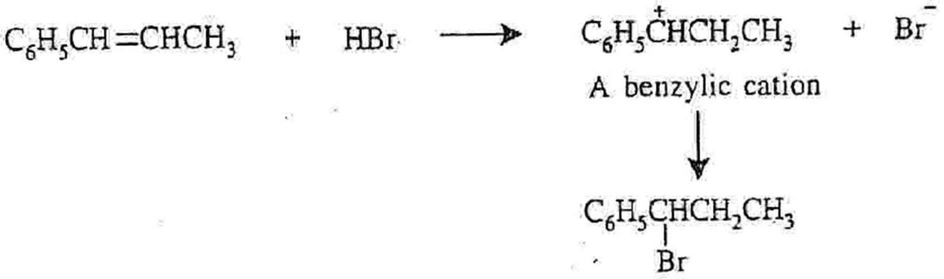
The mechanism for the addition of hydrogen bromide to 1-phenylpropene in the presence of peroxides is a chain mechanism analogous to the one we discussed when we described anti-Markovnikov addition in Section 10.9. The step that determines the orientation of the reaction is the first chain-propagating step. Bromine attacks the second carbon atom of the chain because by doing so the reaction produces a more stable benzylic radical. Had the bromine atom attacked the double bond in the opposite way, a less stable secondary radical would have been formed.



$$C_6H_5CH{=}CHCH_3 + Br\cdot \not\longrightarrow C_6H_5CH(Br){-}\dot{C}HCH_3$$

A secondary radical

(b) Hydrogen bromide addition in the absence of peroxides.



$$C_6H_5CH{=}CHCH_3 + HBr \longrightarrow C_6H_5\overset{+}{C}HCH_2CH_3 + Br^-$$

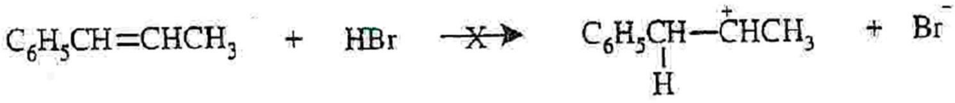
A benzylic cation

$$\downarrow$$

$$C_6H_5CH(Br)CH_2CH_3$$

1-Bromo-1-phenylpropane

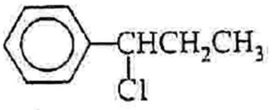
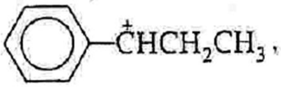
In the absence of peroxides, hydrogen bromide adds through an ionic mechanism. The step that determines the orientation in the ionic mechanism is the first, where the proton attacks the double bond to give the more stable benzylic cation. Had the proton attacked the double bond in the opposite way, a less stable secondary cation would have been formed.

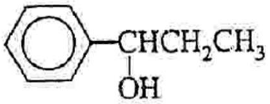


$$C_6H_5CH{=}CHCH_3 + HBr \not\longrightarrow C_6H_5CH(H){-}\overset{+}{C}HCH_3 + Br^-$$

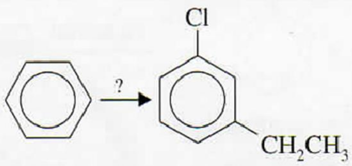
A secondary cation

1-Fenilpropenin aşağıdaki tepkimelerdeki ana ürününün ne olmasını beklersiniz (a) HCl ile tepkimeye girdiğinide (b) Oksiciva katılması–civa atılmasına ayrılmasına uğradığında. ◄ **Problem 15.18**

15.18 (a)  because the more stable carbocation intermediate is the benzylic carbocation, , which then reacts with a chloride ion.

(b)  because the more stable intermediate is a benzylic cation, which then reacts with H_2O.

Problem 15.19 ➤ Benzenden *m*-kloroetilbenzen sentezlemeniz gerektiğini varsayınız.



Benzeni klorlayarak başlayabilir ve sonra CH_3CH_2Cl ve $AlCl_3$ kullanarak Friedel–Crafts alkillemesi yapabilirsiniz veya önce Friedel–Crafts alkillemesi sonra da klorlama yapabilirsiniz. Ancak iki yöntem de istenen ürünü vermez.

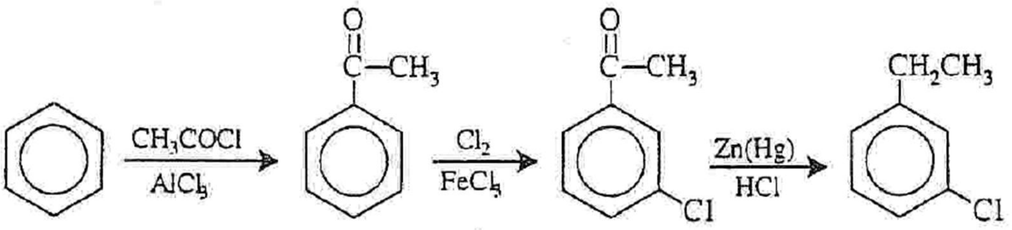
(a) Niçin iki yöntem de istenen ürünü vermez?

(b) Basamaklar doğru sırada yapılırsa bunu başarabilecek üç basamaklı bir yöntem vardır. Bu yöntem nedir?

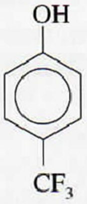
15.19 (a) The first method would fail because introducing the chlorine substituent first would introduce an ortho-para directing group. Consequently, the subsequent Friedel-Crafts reaction would not then take place at the desired meta position.

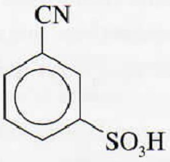
The second method would fail for essentially the same reasons. Introducing the ethyl group first would introduce an ortho-para director, and subsequent ring chlorination would not take place at the desired meta position.

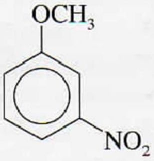
(b) If we introduce an acetyl group first, which we later convert to an ethyl group, we install a meta director. This allows us to put the chlorine atom in the desired position. Conversion of the acetyl group to an ethyl group is then carried out using the Clemmensen reduction.

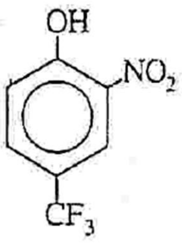


Problem 15.20 ➤ Aşağıdaki bileşiklerin her birisi nitrolandığından elde edilebilecek ana ürünü (veya ürünleri) belirtiniz.

(a)


(b)


(c)


15.20 (a)


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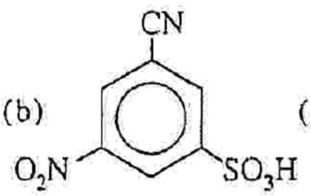
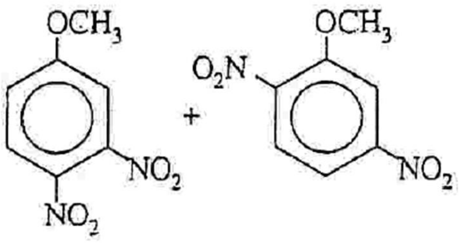
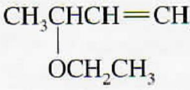


(c)


Problem 15.21 ➤ Aşağıdaki gözlemleri açıklayınız: (a) 1-Kloro-2-büten etanollü ortamda derişik sodyum etoksit çözeltisi ile tepkimeye girdiğinde tepkime hızı allilik halojenürün ve etoksit iyonunun derişimine bağlıdır. Tepkime ürünü olarak yüksek verimle $CH_3CH{=}CHCH_2OCH_2CH_3$ elde edilir. (b) 1-Kloro-2-büten etanol içerisinde çok seyreltik sodyum etoksit çözeltisiyle (veya sadece etanol ile) tepkimeye girdiğinde tepkimenin hızı etoksit iyonunun derişimine bağlı değildir, sadece allilik halojenürün derişimine bağlıdır. Bu koşullarda tepkimede $CH_3CH{=}CHCH_2OCH_2CH_3$ ve

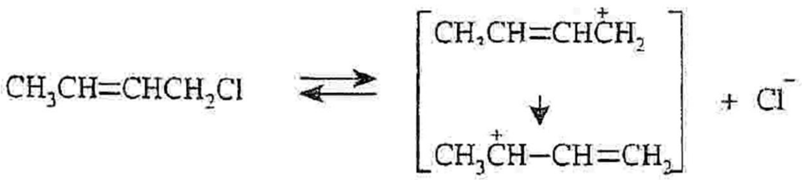

$CH_3\underset{\displaystyle OCH_2CH_3}{\underset{|}{C}}HCH{=}CH_2$ karışımı oluşur.

(c) Eser miktarda su varlığında 1-kloro-2-büten yavaşça 1-kloro-2-büten ve 3-kloro-1-büten karışımına dönüşür.

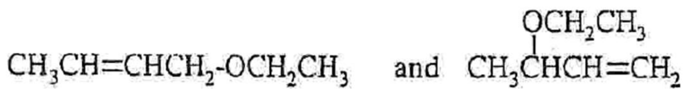
15.21 (a) In concentrated base and ethanol (a relatively nonpolar solvent), the S_N2 reaction is favored. Thus, the rate depends on the concentration of both the alkyl halide and $NaOC_2H_5$. Since no carbocation is formed, the only product is

$$CH_3CH{=}CHCH_2OCH_2CH_3$$

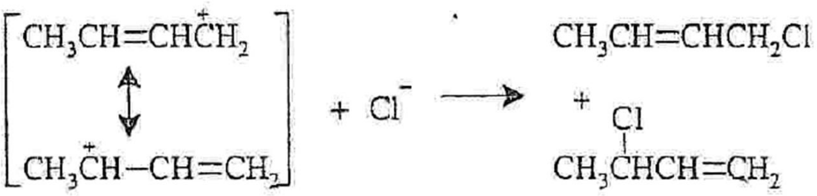
(b) When the concentration of $C_2H_5O^-$ ion is small or zero, the reaction occurs through the S_N1 mechanism. The carbocation that is produced in the first step of the S_N1 mechanism is a resonance hybrid.


$$CH_3CH{=}CHCH_2Cl \rightleftharpoons \left[\begin{array}{c} CH_3CH{=}CH\overset{+}{C}H_2 \\ \downarrow \\ CH_3\overset{+}{C}H{-}CH{=}CH_2 \end{array}\right] + Cl^-$$

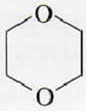
This ion reacts with the nucleophile ($C_2H_5O^-$ or C_2H_5OH) to produce two isomeric ethers


$$CH_3CH{=}CHCH_2\text{-}OCH_2CH_3 \quad \text{and} \quad CH_3\overset{\displaystyle OCH_2CH_3}{\overset{|}{C}}HCH{=}CH_2$$

(c) In the presence of water, the first step of the S_N1 reaction occurs. The reverse of this reaction produces two compounds because the positive charge on the carbocation is distributed over carbon atoms one and three

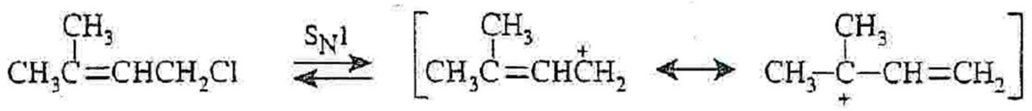

$$\left[\begin{array}{c} CH_3CH{=}CH\overset{+}{C}H_2 \\ \updownarrow \\ CH_3\overset{+}{C}H{-}CH{=}CH_2 \end{array}\right] + Cl^- \longrightarrow \begin{array}{c} CH_3CH{=}CHCH_2Cl \\ + \\ CH_3\overset{\displaystyle Cl}{\overset{|}{C}}HCH{=}CH_2 \end{array}$$

Problem 15.22 ➤ 1-Kloro-3-metil-2-büten su ve dioksan karışımında 1-kloro-2-büteninkinden bin kat daha hızlı hidrolize uğrar. (a) Etkinlikteki bu farklılığın nedeni nedir. (b) Hangi ürünleri elde etmeyi beklersiniz? [Dioksan suyla her oranda karışan halkalı (aşağıda) bir eterdir ve buna benzer tepkimeleri yapmak için yararlı bir yardımcı çözücüdür. Dioksan kanserojendir (yani kansere neden olur) ve bununla birlikte pek çok eter gibi peroksitleri oluşturma eğilimindedir.]



Dioksan

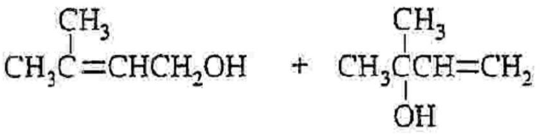
15.22 (a) The carbocation that is produced in the S_N1 reaction is exceptionally stable because one resonance contributor is not only allylic but also tertiary.



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2Cl \xrightleftharpoons{S_N1} \left[CH_3\overset{CH_3}{\overset{|}{C}}=CH\overset{+}{C}H_2 \longleftrightarrow CH_3-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH=CH_2\right]$$

A 3° allylic carbocation

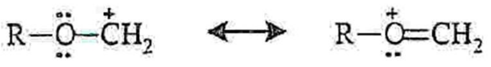
(b)



$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2OH + CH_3\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH=CH_2$$

Problem 15.23 ➤ Pek çok birincil alkil halojenür S_N1 tipi tepkimeye uğramazken, $ROCH_2X$ tipindeki birincil alkil halojenürler S_N1 tipi tepkimeye uğrarlar. $ROCH_2X$ tipindeki halojenürlerin S_N1 tepkimesine uğraması için bir rezonans açıklaması önerebilir misiniz?

15.23 Compounds that undergo reactions by an S_N1 path must be capable of forming relatively stable carbocations. Primary halides of the type $ROCH_2X$ form carbocations that are stabilized by resonance:



$$R-\ddot{\underset{..}{O}}-\overset{+}{C}H_2 \longleftrightarrow R-\overset{+}{\underset{..}{O}}=CH_2$$

Problem 15.24 ➤ Aşağıdaki klorürler, etanol içerisinde, bağıl hızları parantez içinde verilen solvolize uğrarlar. Bu sonuçları nasıl açıklarsınız?

$C_6H_5CH_2Cl$	$(C_6H_5)_2CHCH_3$ $\;\;\;\;\;\;\;\;\;\;\,|$ Cl	$(C_6H_5)_2CHCl$	$(C_6H_5)_3CCl$
(0,08)	**(1)**	**(300)**	**(3 × 10⁶)**

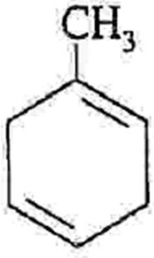
15.24 The relative rates are in the order of the relative stabilities of the carbocations:

$$C_6H_5\overset{+}{C}H_2 < C_6H_5\overset{+}{C}HCH_3 < (C_6H_5)_2\overset{+}{C}H < (C_6H_5)_3\overset{+}{C}$$

The solvolysis reaction involves a carbocation intermediate.

Problem 15.25 ➤ Toluenin Birch indirgenmesi moleküler formülü C_7H_{10} olan bir ürün verir. Ozonlama ve ardından çinko ve suyla indirgeme bu ürünü CH_3COCH_2CHO ve $OHCCH_2CHO$ ya dönüştürür. Birch indirgenme ürününün yapısı nedir?

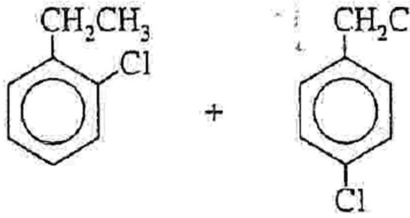
15.25



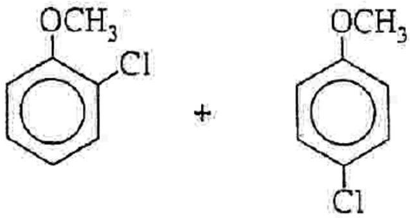
15.26 Aşağıda verilen her bir bileşik Cl_2 ve $FeCl_3$ ile halka klorlanmasına uğratıldığında elde edilebilecek ana ürünü (veya ürünleri) yazınız.

(a) Etilbenzen	**(e)** Nitrobenzen
(b) Anizol ($C_6H_5OCNH_3$)	**(f)** Klorobenzen
(c) Florobenzen	**(g)** Bifenil ($C_6H_5-C_6H_5$)
(d) Benzoik asit	**(h)** Etil fenil eter

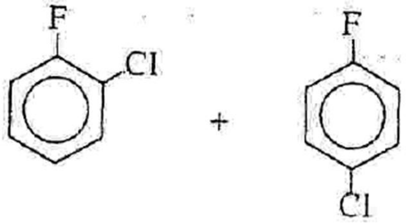
15.26 (a)



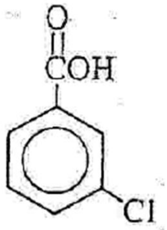
(b)



(c)



(d)



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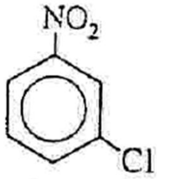
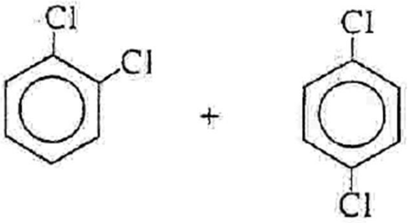
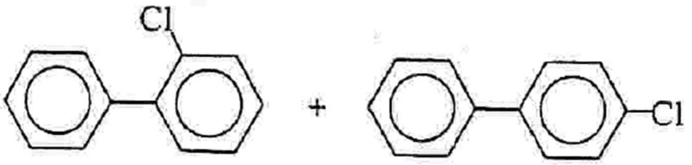


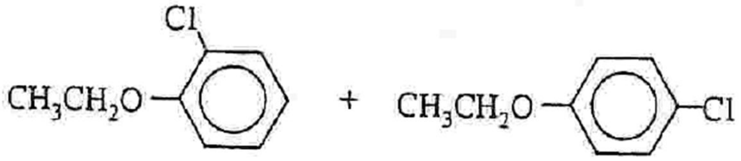
(f)



(g)



(h)



15.27 Aşağıdaki her bir bileşiğin halka nitrolanmasında oluşan ana ürünü (veya ürünleri) yazınız.

(a) Asetanilit ($C_6H_5NHCOCH_3$)

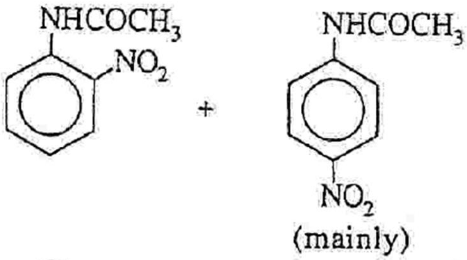
(b) Fenil asetat ($CH_3CO_2C_6H_5$)

(c) 4-Klorobenzoik asit

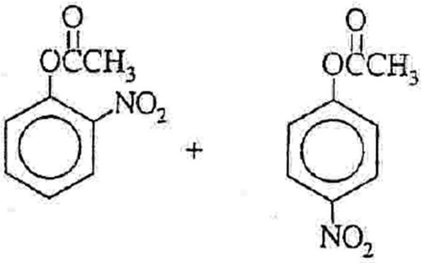
(d) 3-Klorobenzoik asit

(e) $C_6H_5COC_6H_5$

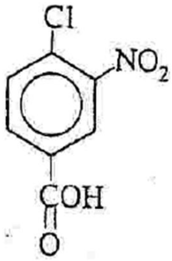
15.27 (a)



(b)



(c)



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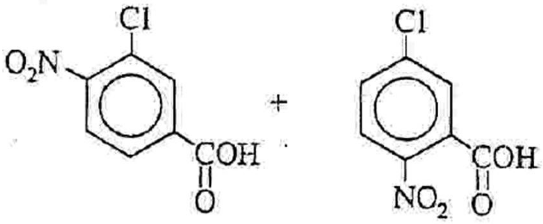

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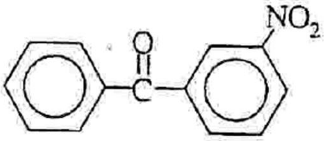


15.28 Aşağıdaki tepkimelerin ana ürünlerini belirtiniz.

(a) Stiren + HCl $\longrightarrow$

(b) 2-Bromo-1-fenilpropan + $C_2H_5ONa \longrightarrow$

(c) $C_6H_5CH_2CHOHCH_2CH_3 \xrightarrow{\text{HA, ısı}}$

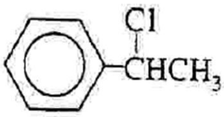
(d) (c)'nin ürünü + HBr $\xrightarrow{\text{peroksitler}}$

(e) (c)'nin ürünü + $H_2O \xrightarrow[\text{ısı}]{\text{HA}}$

(f) (c)'nin ürünü + H_2 (1 eşdeğer mol) $\xrightarrow[25°C]{\text{Pt}}$

(g) (f)'nin ürünü $\xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ HO^-,\ \text{ısı}}$

15.28 (a)



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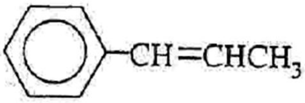

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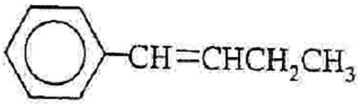

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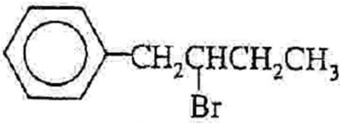

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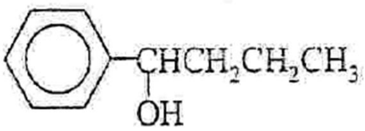

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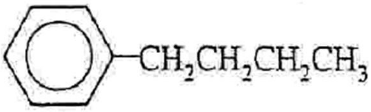

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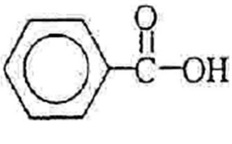
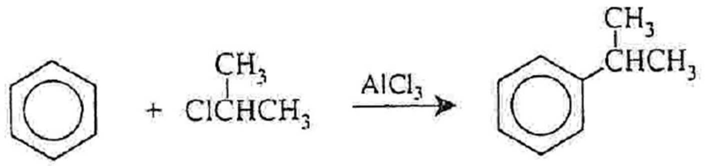


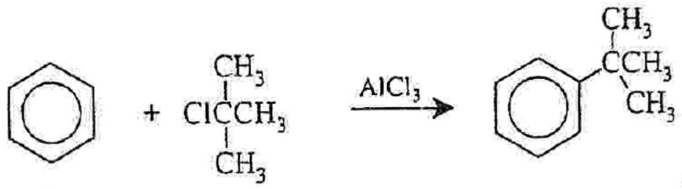
15.29 Benzenle başlayarak, aşağıdaki bileşiklerin her birinin sentezini tasarlayınız.

(a) İzopropilbenzen
(b) *ter*-Bütilbenzen
(c) Propilbenzen
(d) Bütilbenzen
(e) 1-*ter*-Bütil-4-klorobenzen
(f) 1-Fenilsiklopenen
(g) *trans*-2-Fenilsiklopentanol
(h) *m*-Dinitrobenzen
(i) *m*-Bromonitrobenzen
(j) *p*-Bromonitrobenzen
(k) *o*-Klorobenzensülfoik asit
(l) *o*-Kloronitrobenzen
(m) *m*-Nitrobenzensülfoik asit

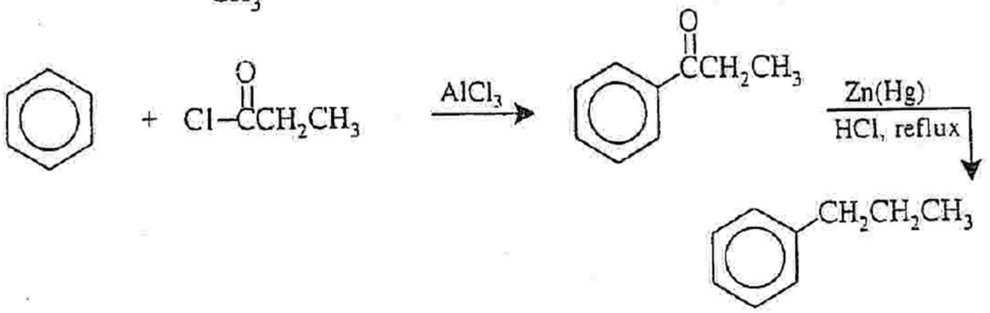
15.29 (a)



(b)

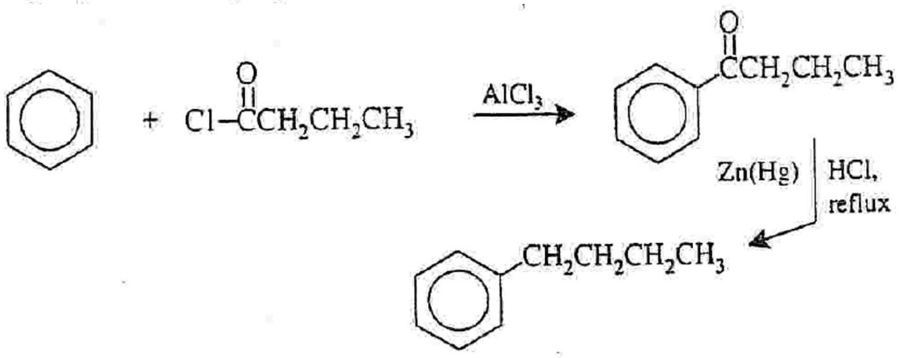


(c)

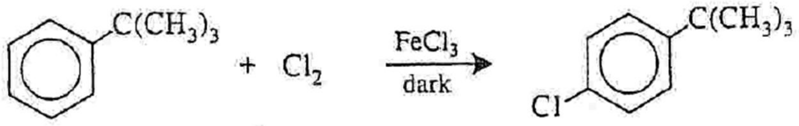


(*Note:* The use of $Cl\text{-}CH_2CH_2CH_3$ in a Friedel-Crafts synthesis gives mainly the rearranged product, isopropylbenzene.)

(d)

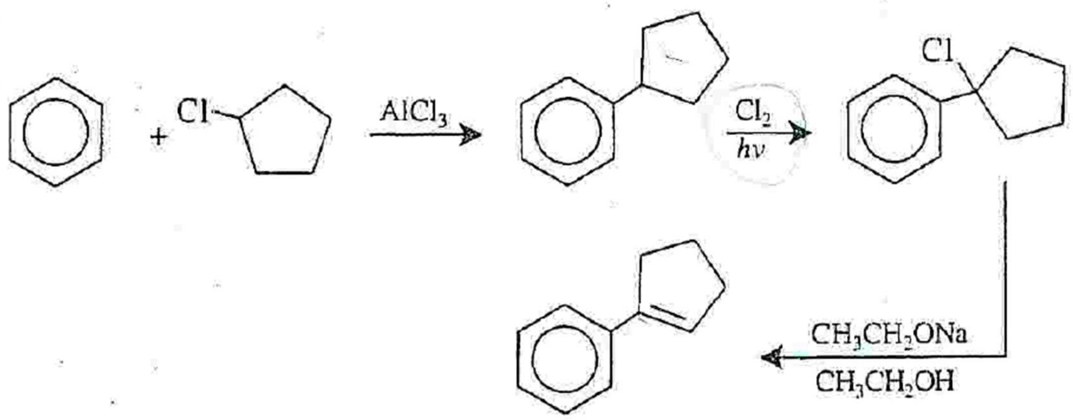


(e)



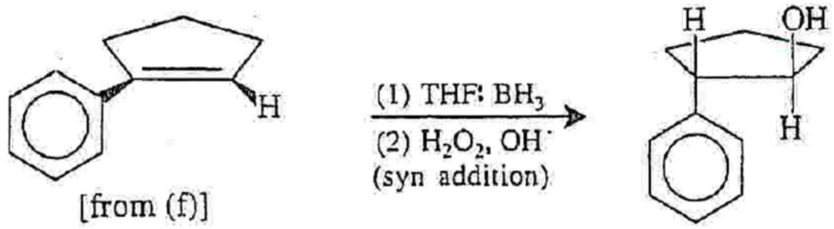
[from (b)]

(f)



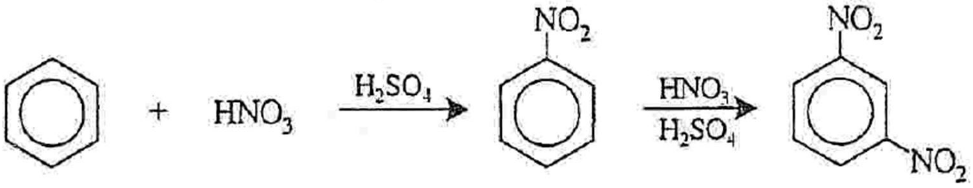
Cl
AlCl$_3$
Cl$_2$
$h\nu$
Cl
CH$_3$CH$_2$ONa
CH$_3$CH$_2$OH

(g)



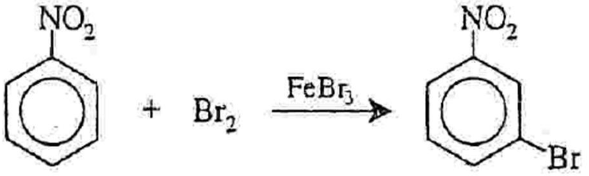
H
[from (f)]
(1) THF: BH$_3$
(2) H$_2$O$_2$, OH$^-$
(syn addition)
H
OH
H

(h)



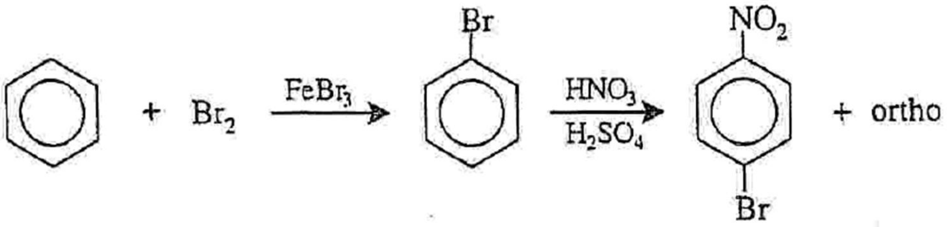
HNO$_3$
H$_2$SO$_4$
NO$_2$
HNO$_3$
H$_2$SO$_4$
NO$_2$
NO$_2$

(i)



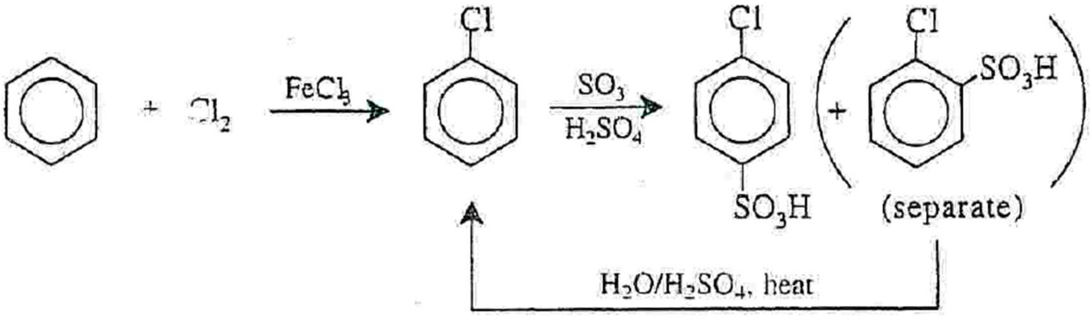
NO$_2$
Br$_2$
FeBr$_3$
NO$_2$
Br

(j)



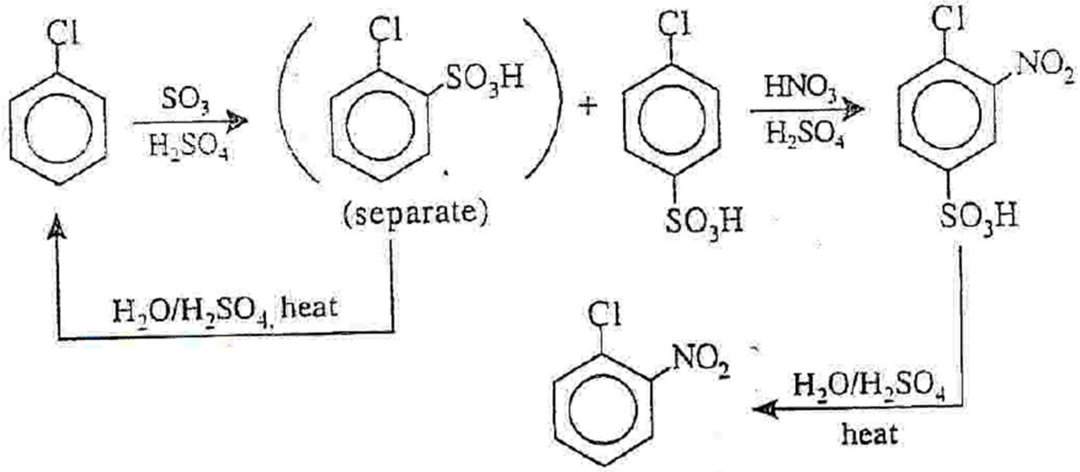
Br$_2$
FeBr$_3$
Br
HNO$_3$
H$_2$SO$_4$
NO$_2$
Br
+ ortho

(k)

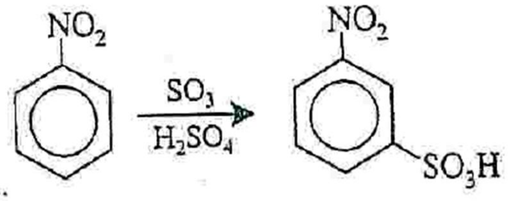


Cl$_2$
FeCl$_3$
Cl
SO$_3$
H$_2$SO$_4$
Cl
SO$_3$H
Cl
SO$_3$H
(separate)
H$_2$O/H$_2$SO$_4$, heat

(l)



(m)



[from (h)]

15.30 Stirenle başlayarak, aşağıdakilerden her birinin sentezini tasarlayınız.

(a) $C_6H_5CHClCH_2Cl$

(b) $C_6H_5CH_2CH_3$

(c) $C_6H_5CHOHCH_2OH$

(d) $C_6H_5CO_2H$

(e) $C_6H_5CHOHCH_3$

(f) $C_6H_5CHBrCH_3$

(g) $C_6H_5CH_2CH_2OH$

(h) $C_6H_5CH_2CH_2D$

(i) $C_6H_5CH_2CH_2Br$

(j) $C_6H_5CH_2CH_2I$

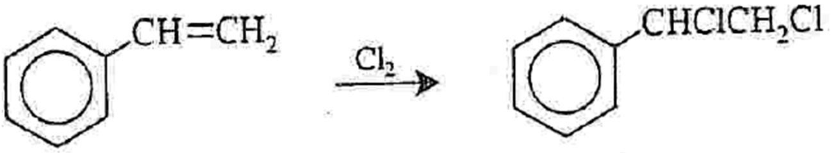
(k) $C_6H_5CH_2CH_2CN$

(l) $C_6H_5CHDCH_2D$

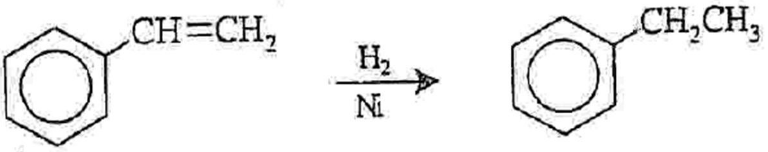
(m) Sikloheksilbenzen

(n) $C_6H_5CH_2CH_2OCH_3$

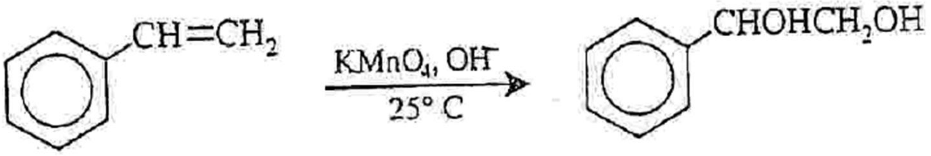
15.30 (a)



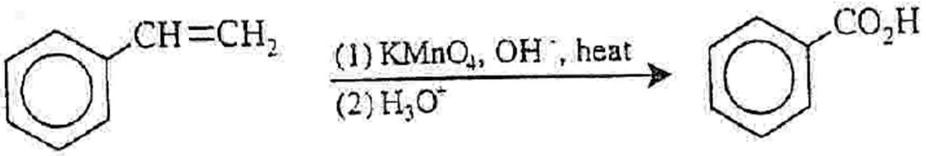
(b)



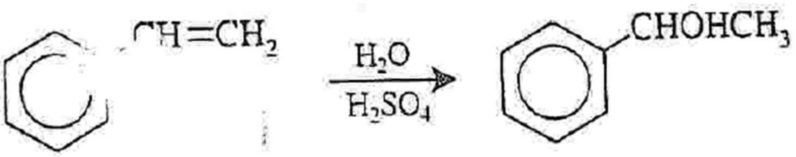
(c)



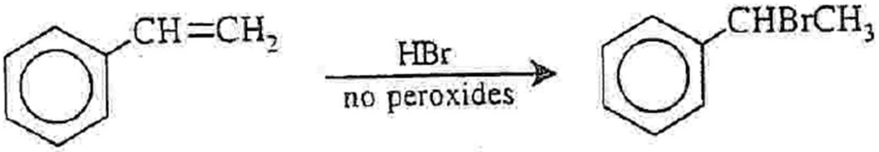
(d)



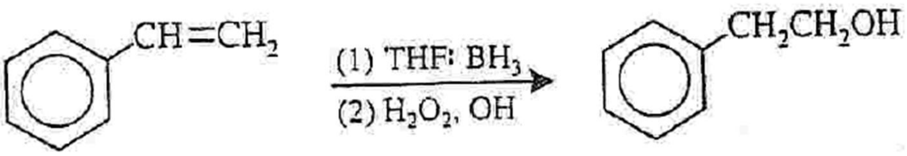
(e)



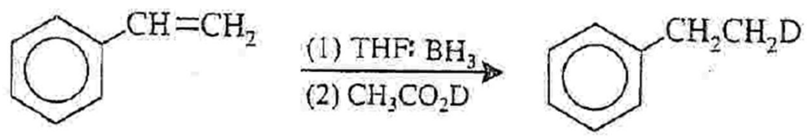
(f)



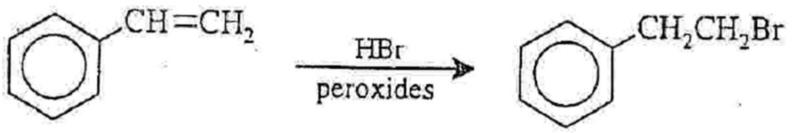
(g)



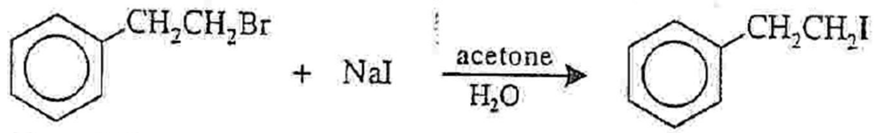
(h)



(i)

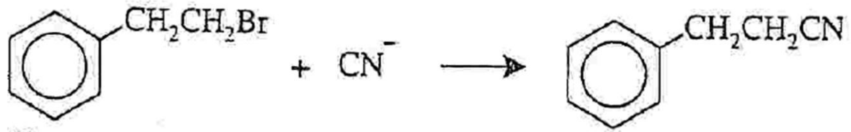


(j)



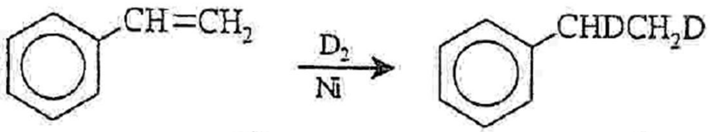
[from (i)]

(k)

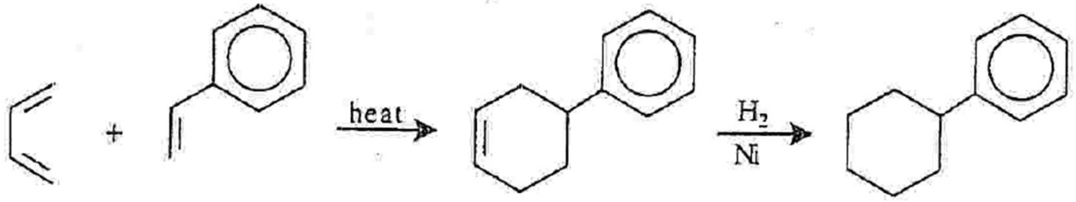


[from (i)]

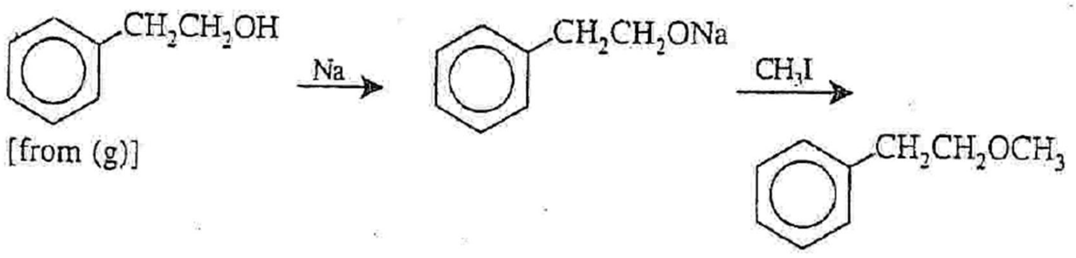
(l)



(m)



(n)

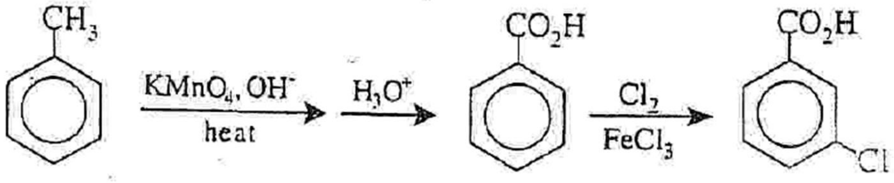


[from (g)]

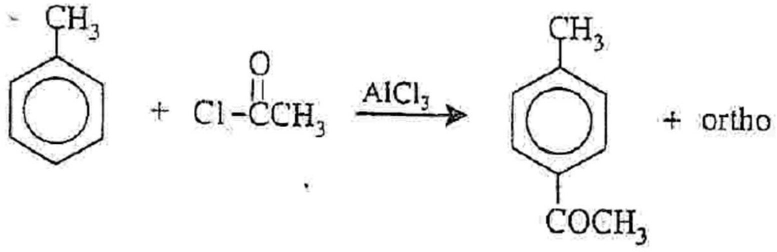
15.31 Toluenle başlayarak, aşağıdakilerin her birinin sentezini tasarlayınız.

- **(a)** *m*-Klorobenzoik asit
- **(b)** *p*-Metilasetofenon
- **(c)** 2-Bromo-4-nitrotoluen
- **(d)** *p*-Bromobenzoik asit
- **(e)** 1-Kloro-3-triklorometilbenzen
- **(f)** *p*-İzopropiltoluen (*p*-kümen)
- **(g)** 1-Sikloheksil-4-metilbenzen
- **(h)** 2,4,6-Trinitrotoluen (TNT)
- **(i)** 4-Kloro-2-nitrobenzoik asit
- **(j)** 1-Bütil-4-metilbenzen

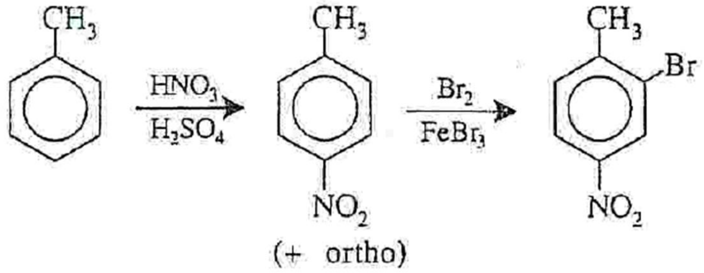
15.31 (a)


CH3
KMnO4, OH-
heat
H3O+
CO2H
Cl2
FeCl3
CO2H
Cl

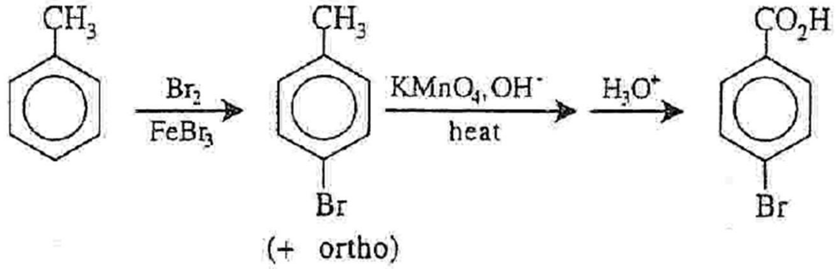
(b)


CH3
+ Cl-C(=O)CH3
AlCl3
CH3
COCH3
+ ortho

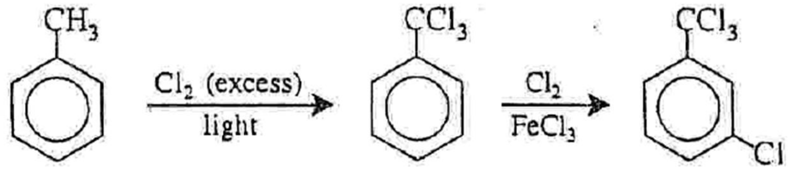
(c)


CH3
HNO3
H2SO4
CH3
NO2
(+ ortho)
Br2
FeBr3
CH3
Br
NO2

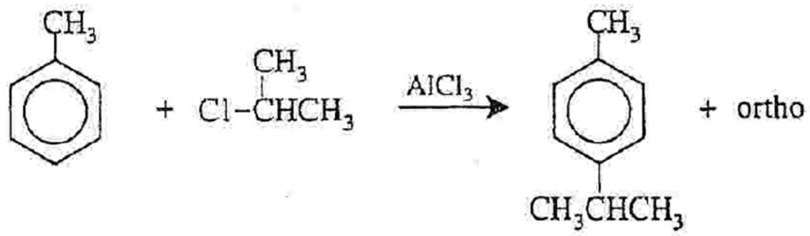
(d)


CH3
Br2
FeBr3
CH3
Br
(+ ortho)
KMnO4, OH-
heat
H3O+
CO2H
Br

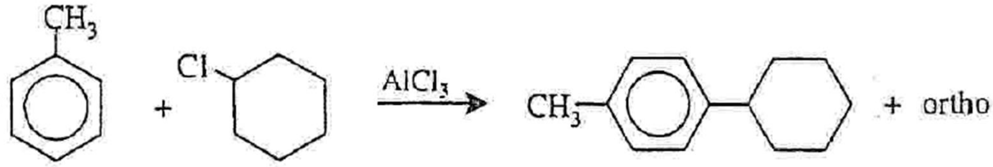
(e)


CH3
Cl2 (excess)
light
CCl3
Cl2
FeCl3
CCl3
Cl

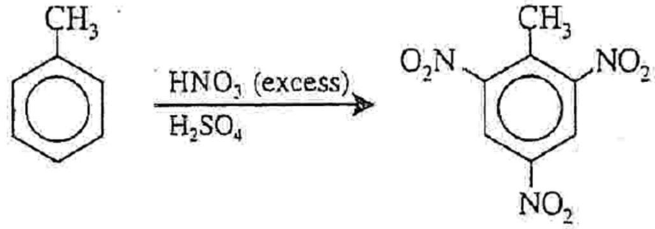
(f)


CH3
+
CH3
Cl–CHCH3
AlCl3
CH3
CH3CHCH3
+ ortho

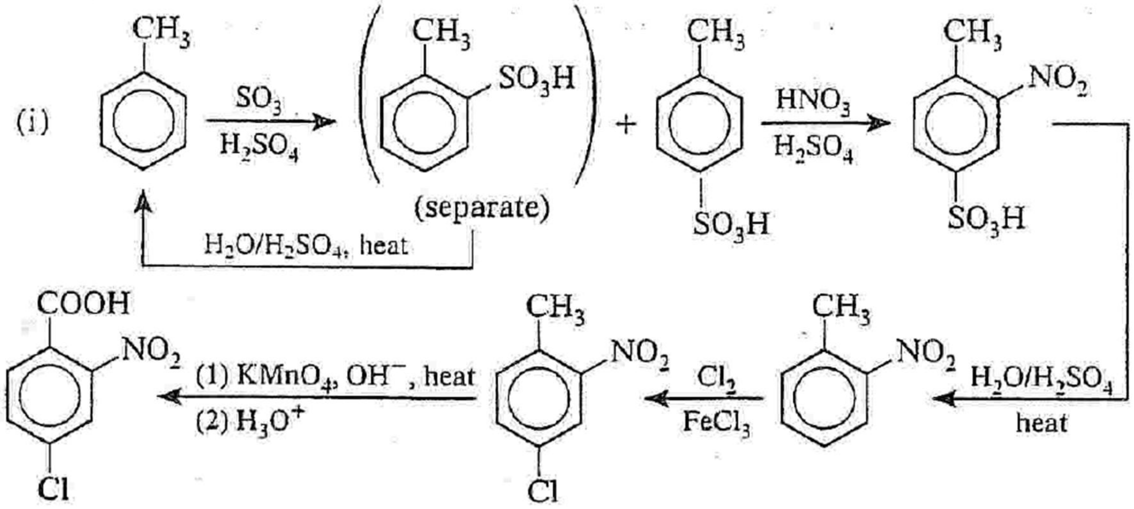
(g)


CH3
+
Cl
AlCl3
CH3
+ ortho

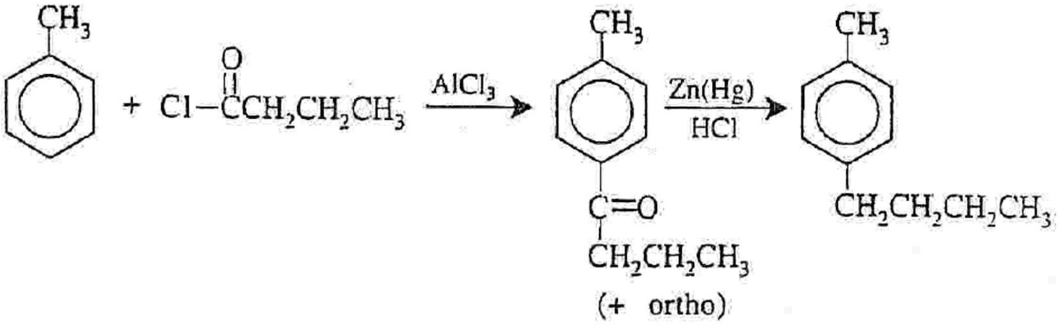
(h)


CH3
HNO3 (excess)
H2SO4
CH3
O2N
NO2
NO2

(i)



(j)



15.32 Anilinle başlayarak, aşağıdakilerin her birinin sentezini tasarlayınız.

(a) *p*-Bromoanilin

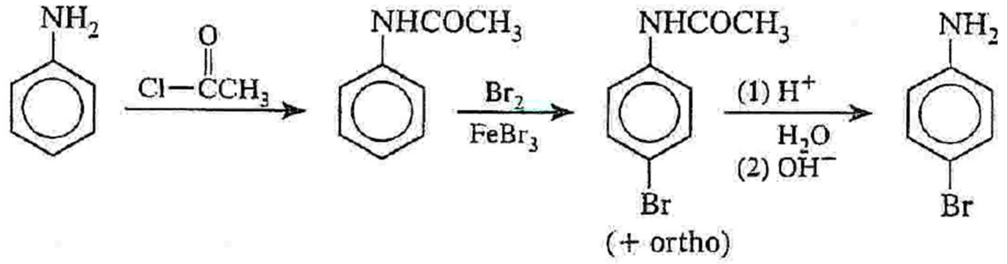
(b) *o*-Bromoanilin

(c) 2-Bromo-4-nitroanilin

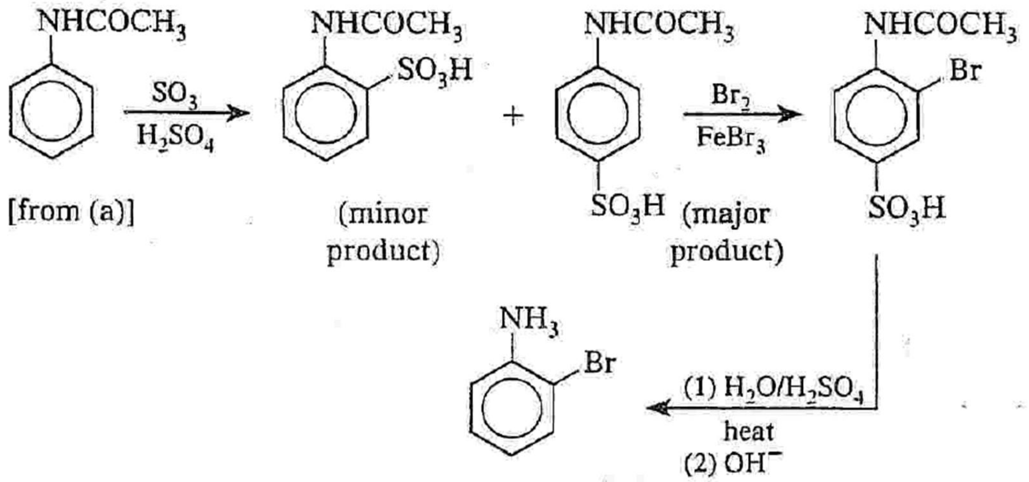
(d) 4-Bromo-2-nitroanilin

(e) 2,4,6-Tribromoanilin

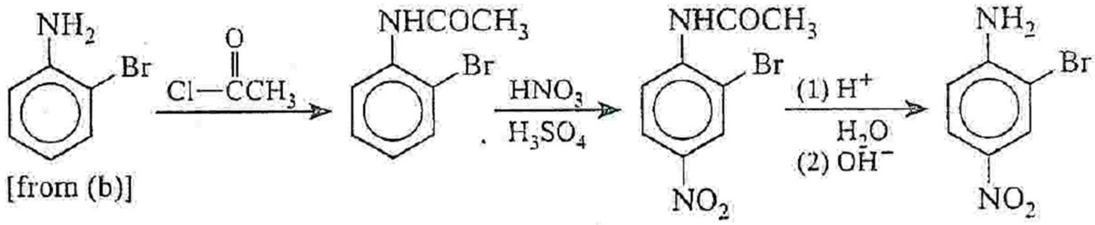
15.32 (a)



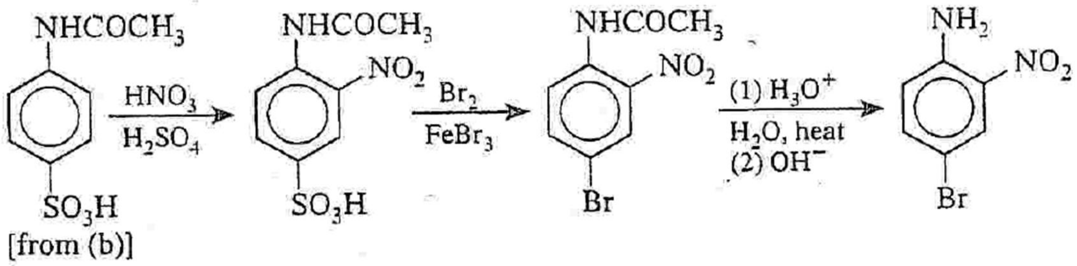
(b)



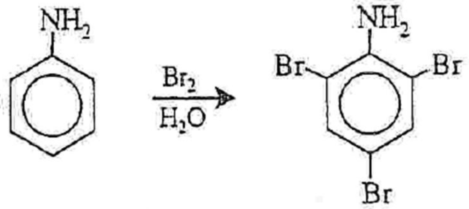
(c)



(d)

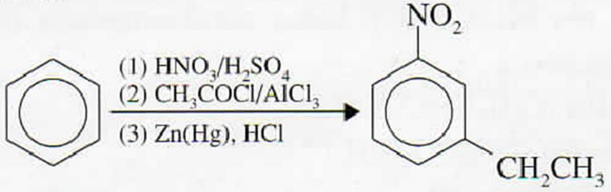


(e)

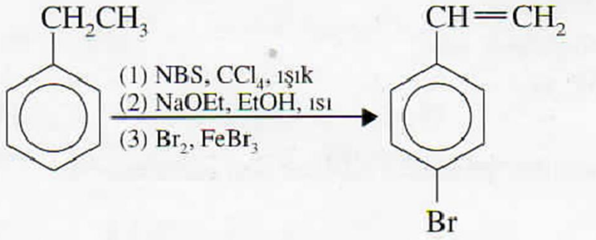


15.33 Aşağıdaki her iki sentez de başarısız olacaktır. Her birinde neyin yanlış olduğunu açıklayınız.

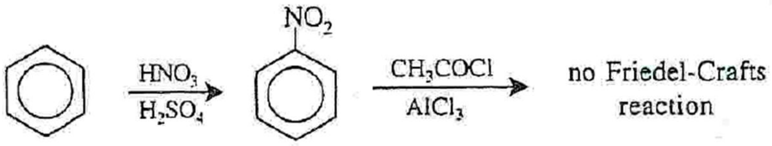
(a)



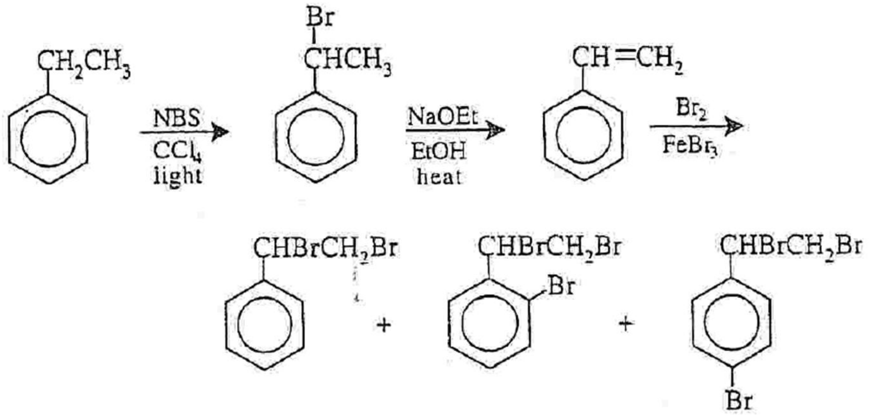
(b)



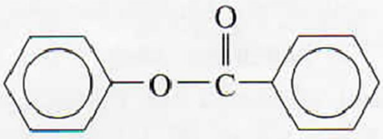
15.33 (a) Step (2) will fail because a Friedel-Crafts reaction will not take place on a ring that bears an $-NO_2$ group (or any meta director).



(b) The last step will first brominate the double bond.

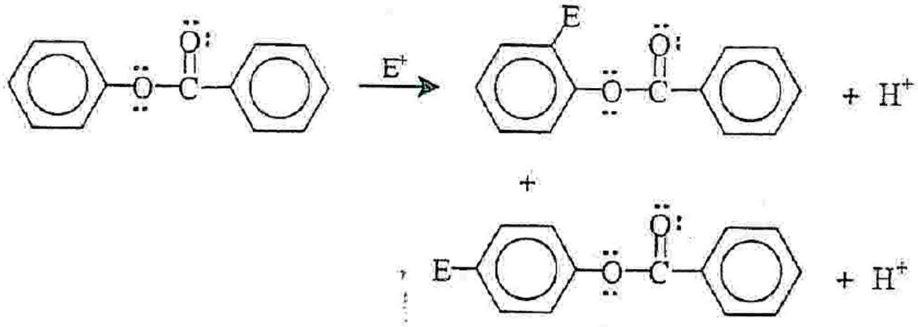


15.34 Fenilbenzoatın bir halkası diğerinden daha kolay elektrofilik aromatik yer değiştirmeye uğrar. **(a)** Bu halka hangisidir? **(b)** Cevabınızı açıklayınız.



Fenil benzoat

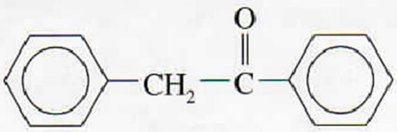
15.34 (a) Electrophilic aromatic substitution will take place as follows:



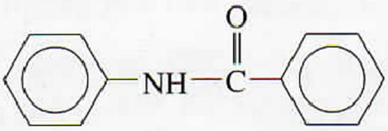
(b) The ring directly attached to the oxygen atom is activated toward electrophilic attack because the oxygen atom can donate an unshared electron pair to it and stabilize the intermediate arenium ion when attack occurs at the ortho or para position.

15.35 Aşağıdaki bileşikler Br_2 ve $FeBr_3$ ile halka bromlamasına uğratıldıklarında hangi ürünün (veya ürünleri) oluşmasını beklersiniz?

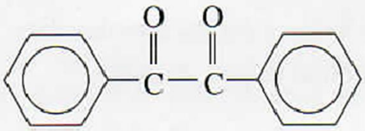
(a)



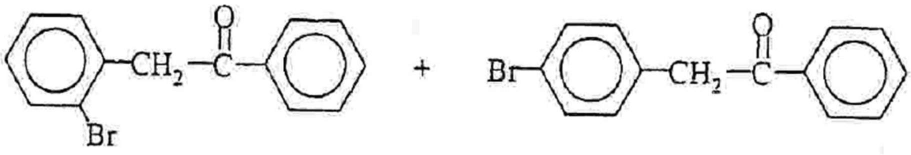
(b)



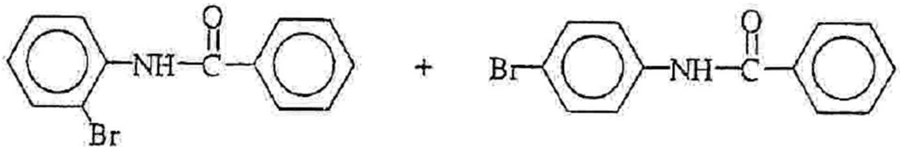
(c)



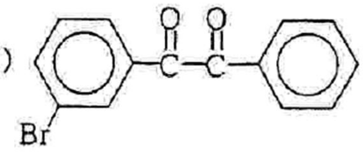
15.35 (a)



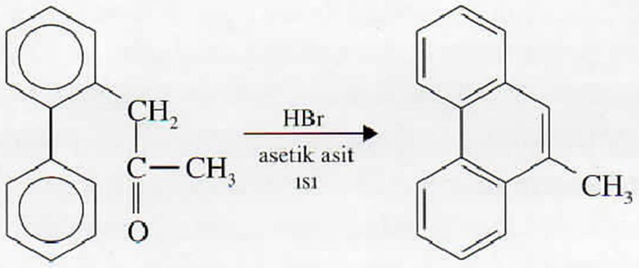
(b)



(c)



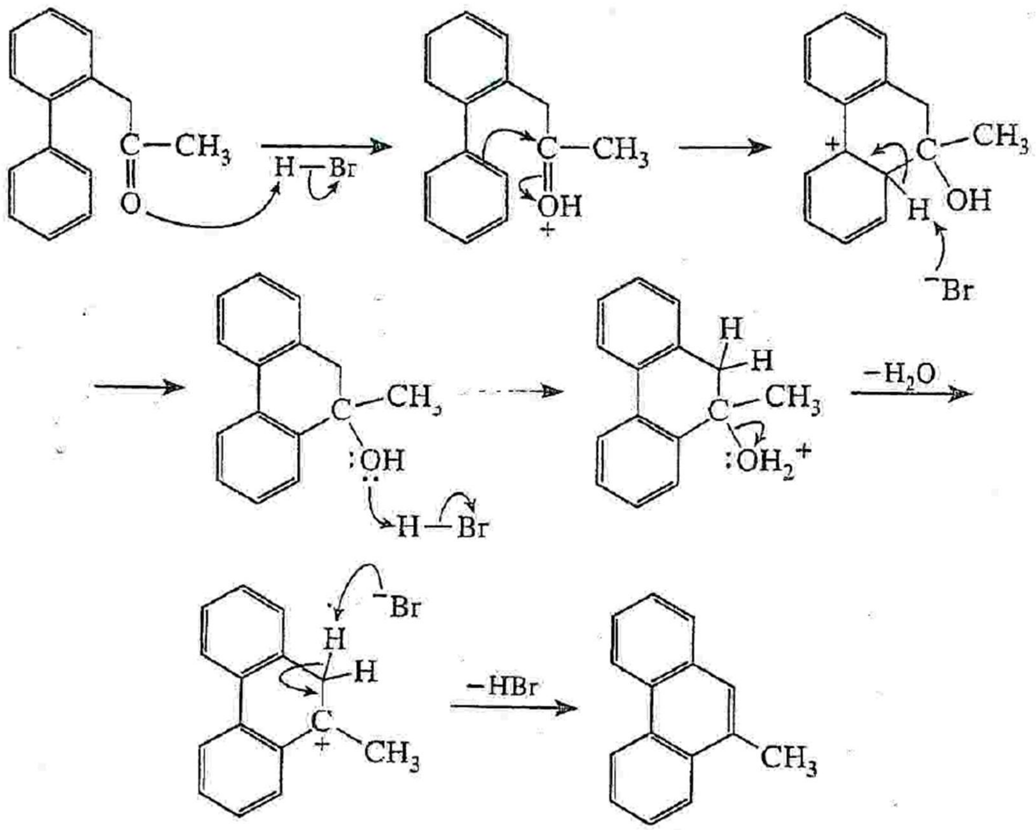
15.36 Pek çok polisiklik aromatik bileşik **Bradsher tepkimesi** veya **aromatik siklodehidrasyon** olarak bilinen halkalaşma tepkimesi ile sentezlenmiştir. Bu yöntem 9-metilfenantrenin aşağıdaki sentezi ile gösterilebilir.



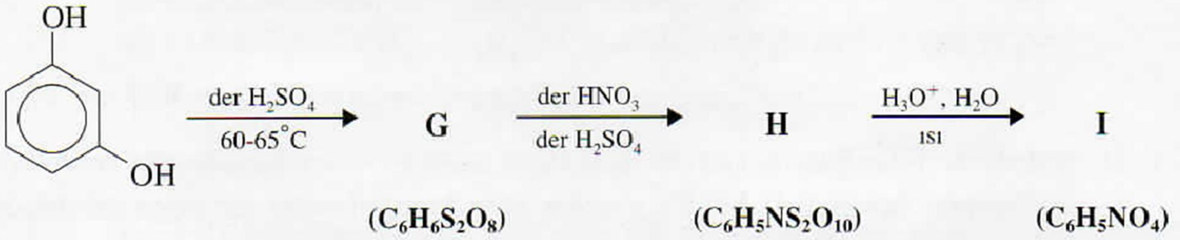
9-Metilfenantren

Bu tepkimede arenyum iyonu bir ara üründür ve son basamak alkolün dehidrasyonunu içerir. Bradsher tepkimesi için verilen yukarıdaki örnek için mantıklı bir mekanizma öneriniz.

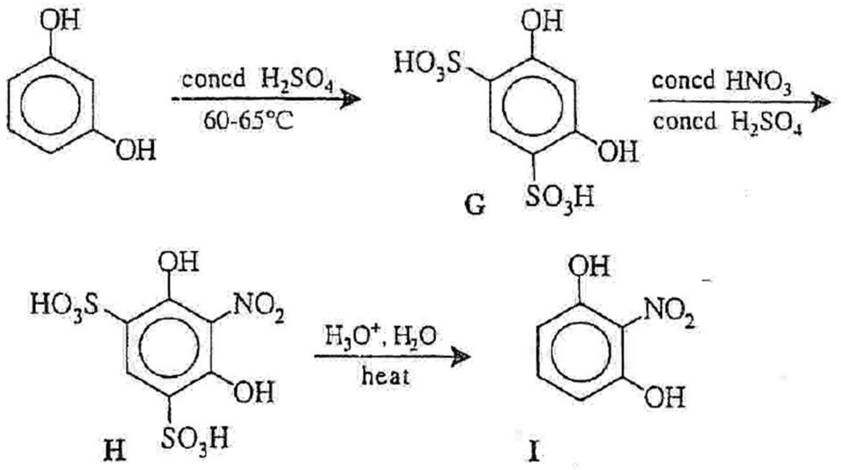
15.36



15.37 **G–I** Bileşiklerinin yapılarını bulunuz.

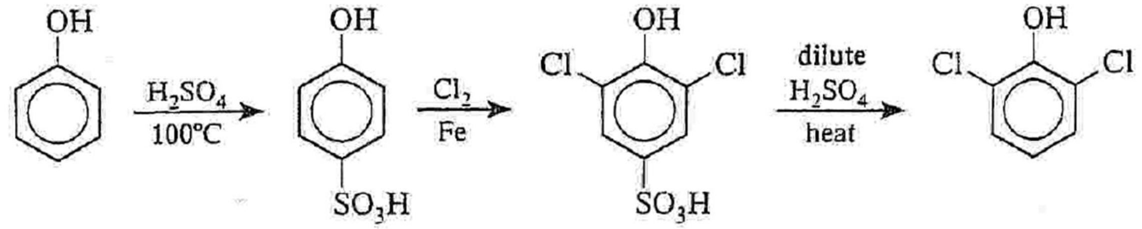


15.37 This problem serves as another illustration of the use of a sulfonic acid group as a blocking group in a synthetic sequence. Here we are able to bring about nitration between two meta substituents.



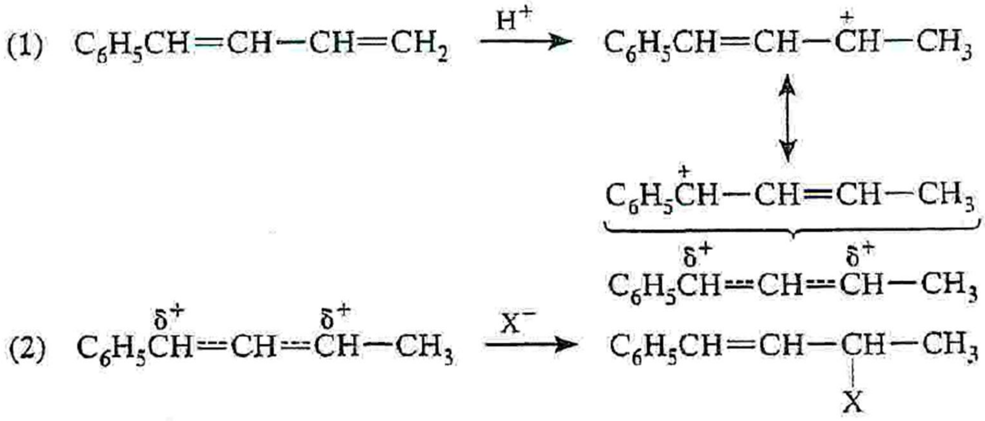
15.38 2,6-Diklorofenol iki kene türünün (*Amblyomma americanum* ve *A. maculatum*) dişilerinden izole edilmiştir ve bu maddenin bir seks çekicisi olduğu bilinmektedir. Her bir dişi keneden yaklaşık 5 ng 2,6-diklorofenol elde edilir. Bu miktardan daha fazlasına ihtiyacınız olduğunu varsayınız ve bunun içinde 2,6-diklorofenolün fenolden başlayan bir sentezini tasarlayınız (*İpucu*: Fenol 100°C'da sülfolandığında ürün başlıca *p*-hidroksibenzensülfonik asittir.)

15.38



15.39 Hidrojen halojenürün (hidrojen bromür veya hidrojen klorür) 1-fenil-1,3-bütadiene katılması (sadece) 1-fenil-3-halo-1-büten verir. **(a)** Bu ürünün oluşumunu açıklayan bir mekanizma yazınız. **(b)** Bu, bütadien sistemine 1,4 veya 1,2 katılması mıdır? **(c)** Tepkimenin ürünü en kararlı karbokatyon ara ürünü oluşumu ile uyumlu mudur? **(d)** Tepkime kinetik kontrollü mü yoksa denge kontrollü müdür? Açıklayınız.

15.39 (a)

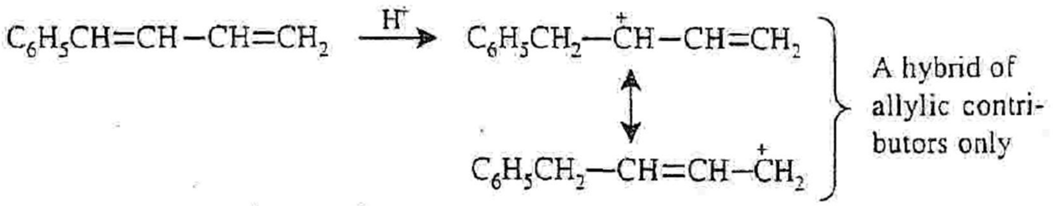


$$(1)\quad C_6H_5CH{=}CH{-}CH{=}CH_2 \xrightarrow{H^+} \underbrace{C_6H_5CH{=}CH{-}\overset{+}{C}H{-}CH_3 \longleftrightarrow C_6H_5\overset{+}{C}H{-}CH{=}CH{-}CH_3}_{C_6H_5\overset{\delta^+}{C}H \text{=\!=} CH \text{=\!=} \overset{\delta^+}{C}H{-}CH_3}$$

$$(2)\quad C_6H_5\overset{\delta^+}{C}H \text{=\!=} CH \text{=\!=} \overset{\delta^+}{C}H{-}CH_3 \xrightarrow{X^-} C_6H_5CH{=}CH{-}\underset{X}{CH}{-}CH_3$$

(b) 1,2 Addition.

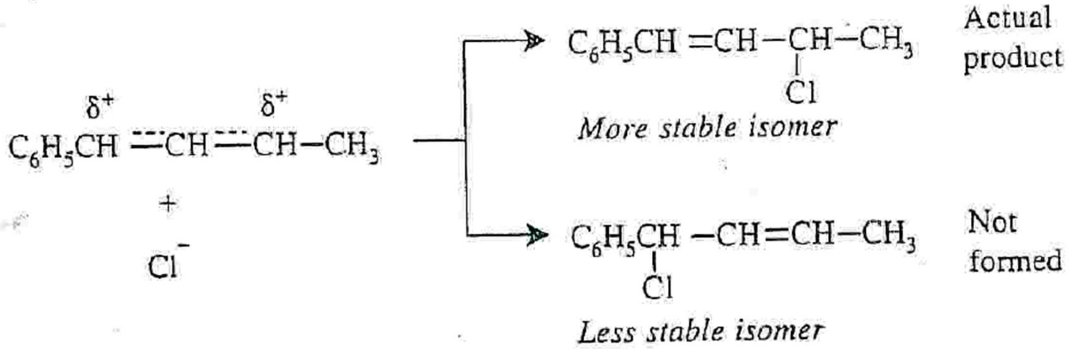
(c) Yes. The carbocation given in (a) is a hybrid of *secondary allylic and benzylic* contributors and is therefore more stable than any other possibility; for example,



$$C_6H_5CH{=}CH{-}CH{=}CH_2 \xrightarrow{H^+} \left.\begin{array}{c} C_6H_5CH_2{-}\overset{+}{C}H{-}CH{=}CH_2 \\ \updownarrow \\ C_6H_5CH_2{-}CH{=}CH{-}\overset{+}{C}H_2 \end{array}\right\}$$

A hybrid of allylic contributors only

(d) Since the reaction produces only *the more stable isomer*—that is, the one in which the double bond is conjugated with the benzene ring—the reaction is likely to be under equilibrium control:



$$C_6H_5\overset{\delta^+}{C}H \overset{\cdots}{=} CH \overset{\cdots}{=} \overset{\delta^+}{C}H-CH_3 \quad + \quad Cl^-$$

$$\longrightarrow C_6H_5CH=CH-\underset{\displaystyle Cl}{\underset{|}{C}H}-CH_3$$

More stable isomer — Actual product

$$\longrightarrow C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}H}-CH=CH-CH_3$$

Less stable isomer — Not formed

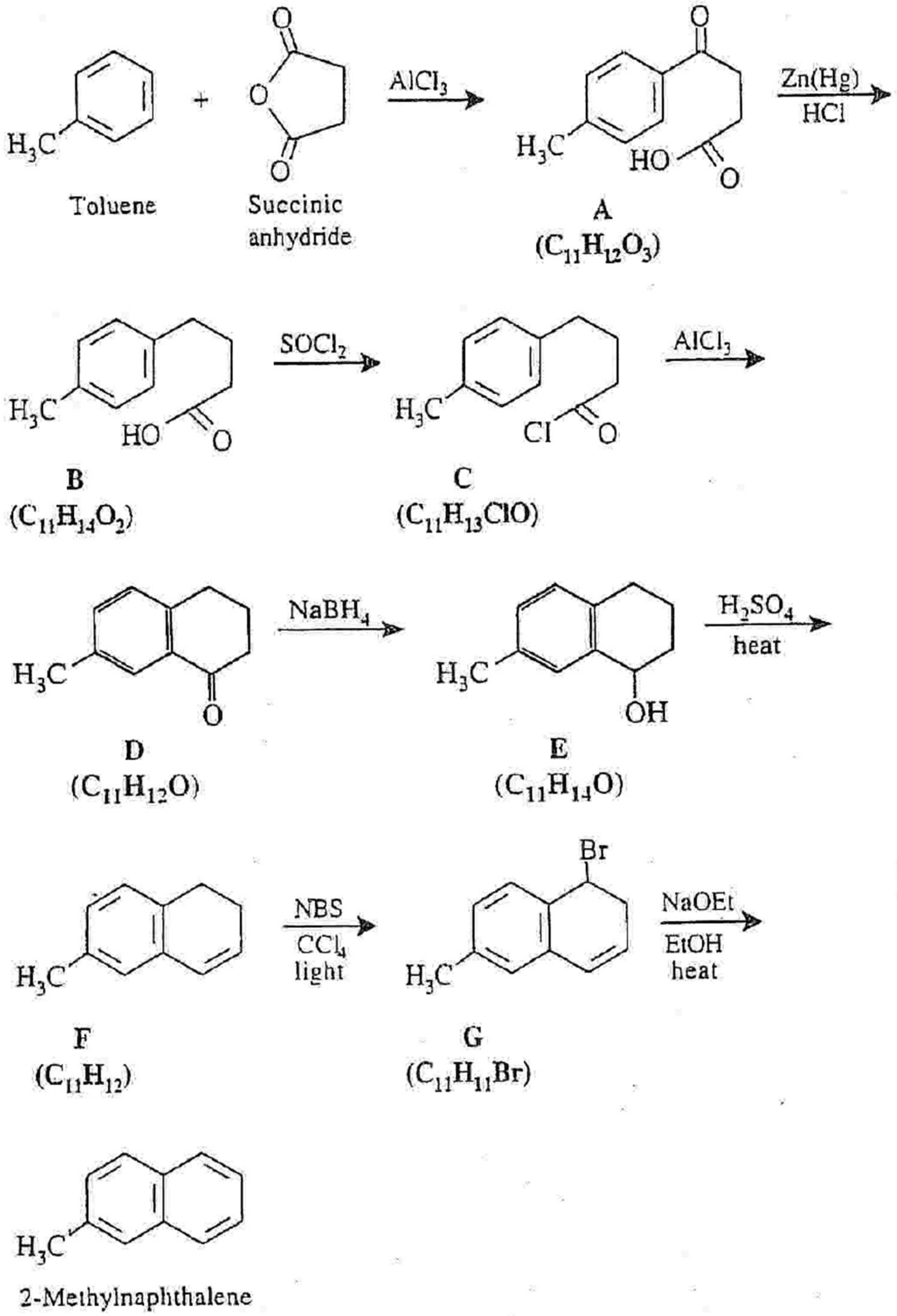
15.40 2-Metilnaftalin toluenden aşağıdaki tepkime sırası ile sentezlenebilir. Her bir ara ürünün yapısını yazınız.

$$\text{Toluen} + \text{süksinik anhidrit} \xrightarrow{AlCl_3} \underset{(C_{11}H_{12}O_3)}{\mathbf{A}} \xrightarrow[HCl]{Zn(Hg)} \underset{(C_{11}H_{14}O_2)}{\mathbf{B}}$$

$$\xrightarrow{SOCl_2} \underset{(C_{11}H_{13}ClO)}{\mathbf{C}} \xrightarrow{AlCl_3} \underset{(C_{11}H_{12}O)}{\mathbf{D}} \xrightarrow{NaBH_4} \underset{(C_{11}H_{14}O)}{\mathbf{E}}$$

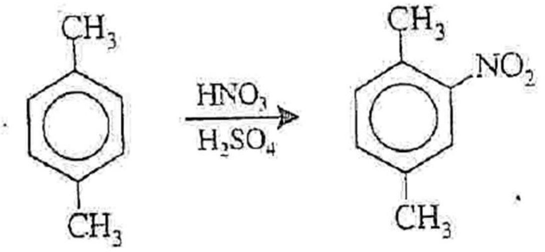
$$\xrightarrow[\text{ısı}]{H_2SO_4} \underset{(C_{11}H_{12})}{\mathbf{F}} \xrightarrow[CCl_4,\ \text{ışık}]{NBS} \underset{(C_{11}H_{11}Br)}{\mathbf{G}} \xrightarrow[EtOH \atop \text{ısı}]{NaOEt} \text{2-Metilnaftalin}$$

15.40



15.41 Dimetilbenzenin (bir ksilen) halka nitrolanması sadece bir nitrodimetilbenzen verir. Bu dimetilbenzenin yapısı nedir?

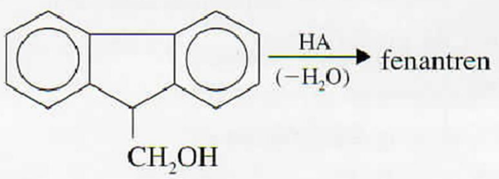
15.41



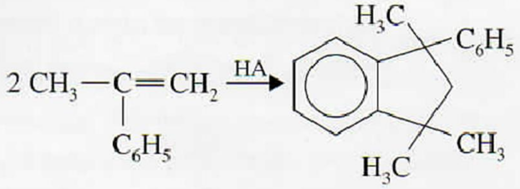
(only possible mononitro product)

15.42 Aşağıdaki tepkimeleri açıklayan mekanizmaları yazınız.

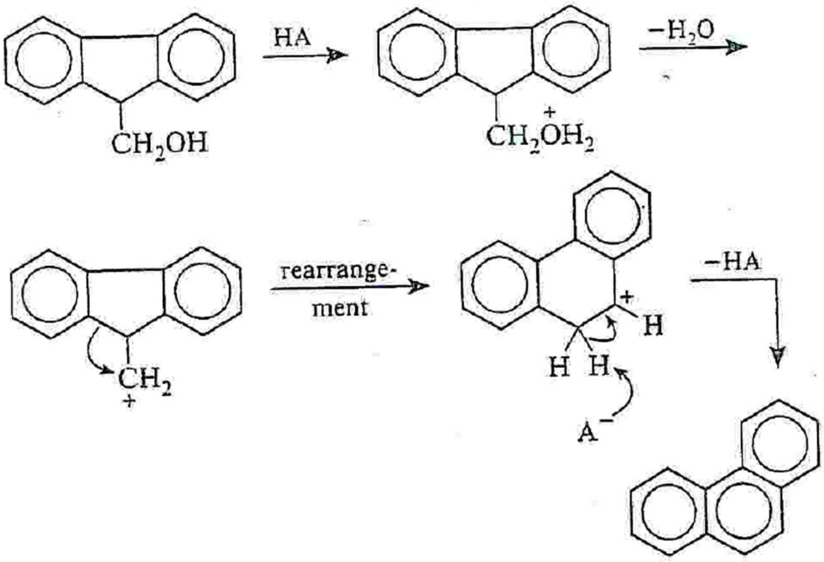
(a)



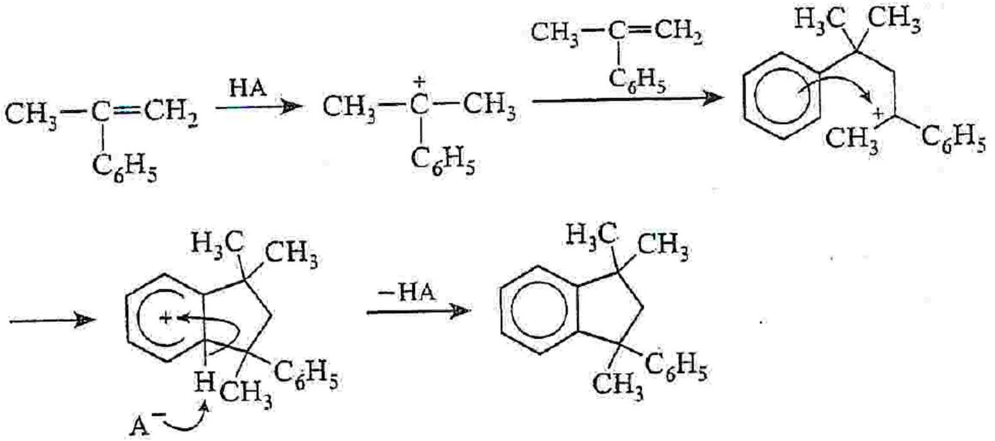
(b)



15.42 (a)

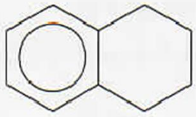


(b)

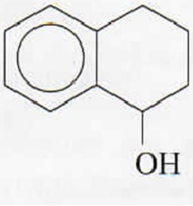


15.43 α-Tetralon ile başlayarak aşağıdakilerin her birini nasıl sentezleyeceğinizi gösteriniz (Altbölüm 15.9).

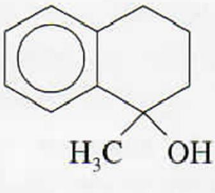
(a)



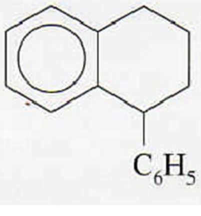
(b)



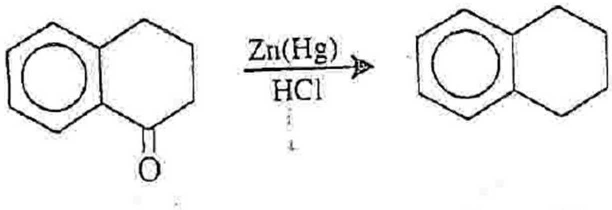
(c)



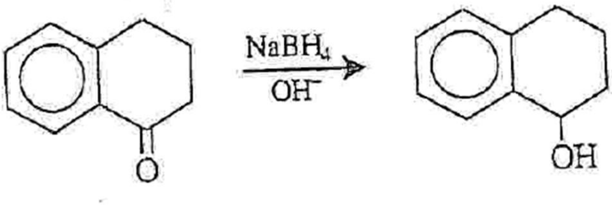
(d)

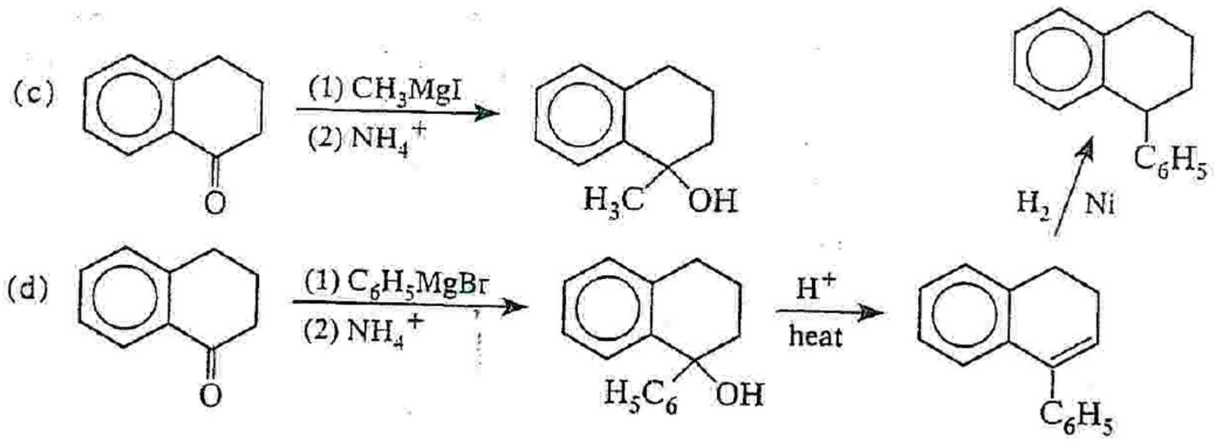


15.43 (a)

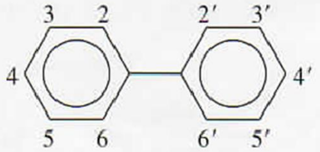


(b)



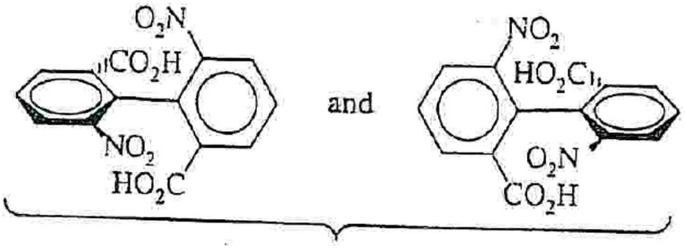


15.44 Fenilbenzen ($C_6H_5 — C_6H_5$) bileşiği *bifenil* olarak isimlendirilir ve halkalar aşağıdaki gibi numaralandırılır.



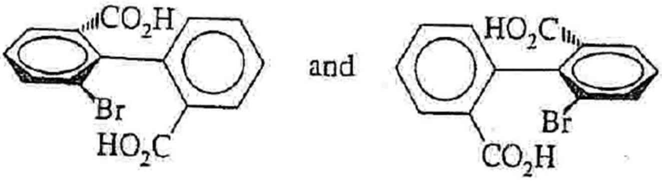
Sübstitüe bifeniller hakkında aşağıdaki soruları cevaplamak için modeller kullanınız. **(a)** Belirli büyük gruplar *orto* konumlarının üç veya dördünde bulunursa (yani, 2, 6, 2′ ve 6′) sübstitüe bifenil enantiyomerik yapılarda bulunabilir. Enantiyomerik yapılarda bulunan bifenillere örnek, 2-NO_2, 6-CO_2H, 2′-NO_2, 6′-CO_2H sübstitüentleri bulunduran bifenildir. **(b)** Bundan sorumlu olan etkenler nelerdir. (*b*) 2-Br, 6-CO_2H, 6′-H bulunduran bifenilin enantiyomerik yapılarda bulunmasını bekler misiniz? **(c)** 2-NO_2, 6-NO_2, 2′-CO_2H, 6′-Br bulunduran bifenil enantiyomerik yapılara ayrılamaz (yarılamaz) Niçin? Açıklayınız.

15.44 (a) Large ortho substituents prevent the two rings from becoming coplanar and prevent rotation about the single bond that connects them. If the correct substitution patterns are present, the molecule as a whole will be chiral. Thus, enantiomeric forms are possible even though the molecules do not have a stereocenter. The compound with 2-NO_2, 6-CO_2H, 2′-NO_2, 6′-CO_2H is an example.

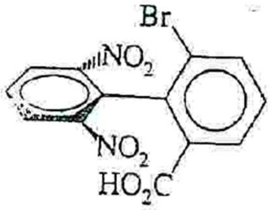


These molecules are nonsuperposable mirror images and, thus, are enantiomers.

(b) Yes

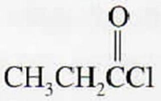


(c) This molecule has a plane of symmetry.



The plane of the page is a plane of symmetry.

15.45 **A–G** Bileşiklerinin yapılarını (uygun olduğunda stereokimyasıyla) yazınız.



(a) Benzen + $CH_3CH_2\overset{\overset{\large O}{\|}}{C}Cl \xrightarrow{AlCl_3}$ **A** $\xrightarrow[0°C]{PCl_5}$ **B** $(C_9H_{10}Cl_2) \xrightarrow[\text{mineral yağ, ısı}]{2\ NaNH_2}$

C $(C_9H_8) \xrightarrow{H_2,\ Ni_2B\ (P\text{-}2)}$ **D** (C_9H_{10})

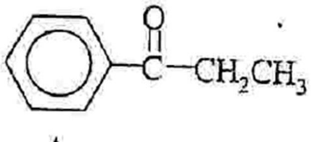
(*İpucu*: C bileşiğinin ¹H NMR spektrumu δ 7,20'de bir çoklu (5H) ve δ 2,0'da bir birli (3H) içerir.

(b) **C** $\xrightarrow[(2)\ H_2O]{(1)\ Li,\ \text{sıvı}\ NH_3}$ **E** (C_9H_{10})

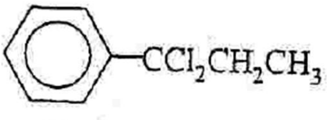
(c) **D** $\xrightarrow[2–5°C]{Br_2,\ CCl_4}$ **F** + enantiyomer (ana ürünler)

(d) **E** $\xrightarrow[2–5°C]{Br_2,\ CCl_4}$ **G** + enantiyomer (ana ürünler)

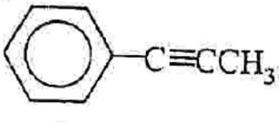
15.45 (a)



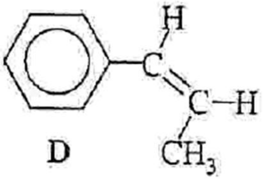
A



B

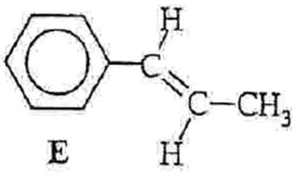


C



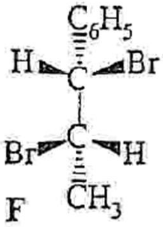
D

(b)



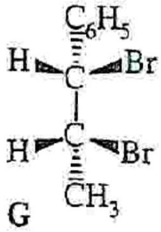
E

(c)



F

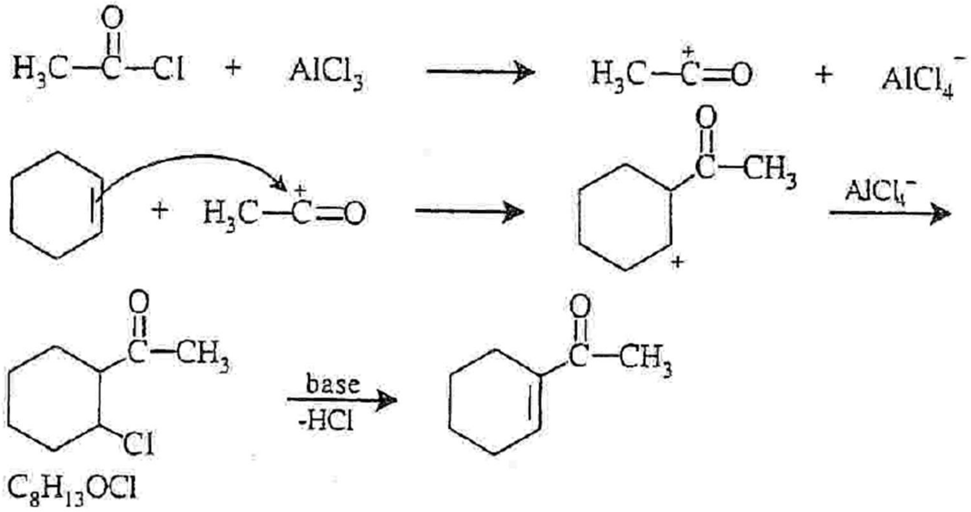
(d)



G

15.46 Sikloheksenin asetil klorür ve $AlCl_3$ ile etkileştirilmesi molekül formülü $C_8H_{13}ClO$ olan bir ürün verir. Bu ürünün bir baz ile etkileştirilmesi ise 1-asetilsiklohekseni oluşturur. Bu tepkime sıralarının her iki basamağı için mekanizma öneriniz.

15.46



$H_3C-C(=O)-Cl + AlCl_3 \longrightarrow H_3C-\overset{+}{C}{=}O + AlCl_4^-$
$H_3C-\overset{+}{C}{=}O$
$AlCl_4^-$
base
-HCl
$C_8H_{13}OCl$

15.47 *ter*-Bütil grubu, bazı aromatik bileşiklerin sentezlerinde bir kapatıcı grup olarak kullanılır. **(a)** ter-Bütil grubunu nasıl katarsınız? **(b)** Nasıl çıkarırsınız? **(c)** Bir kapatıcı grup olarak *ter*-bütil grubunun SO_3H grubuna göre olumlu yanları nelerdir?

15.47 (a and b) The *tert*-butyl group is easily introduced by any of the variations of the Friedel-Crafts alkylation reaction, and, because of the stability of the *tert*-butyl cation, it is easily removed under acidic conditions.

(c) In contrast to the $-SO_3H$ group often used as a blocking group, $-C(CH_3)_3$ activates the ring to further electrophilic substitution.

15.48 Toluen oda sıcaklığında sülfolandığında (derişik H_2SO_4 ile) tepkime ürününün yaklaşık %95'i orto ve para yer değiştirme ürünleridir. Daha yüksek sıcaklık (150–200°C) ve daha uzun tepkime süresi uygulanırsa, ürünün yaklaşık %95'i meta (başlıca) ve para yer değiştirme ürünüdür. Bu farklılığın nedenini açıklayınız. (*İpucu: m*–Toluensülfonik asit en kararlı izomerdir).

15.48 At the lower temperature, the reaction is kinetically controlled, and the usual o/p directive effects of the $-CH_3$ group are observed. At higher temperatures, the reaction is thermodynamically controlled. At reaction times long enough for equilibrium to be reached, the most stable isomer, *m*-toluenesulfonic acid, is the principal product.

15.49 Bir C—D bağının kırılması bir C—H bağının kırılmasından zordur ve sonuçta C—D bağlarının kırıldığı tepkimeler, C—H bağının kırıldığı tepkimelerden daha yavaştır. Perdöteryobenzenin (C_6D_6) normal benzenle (C_6H_6) aynı hızda nitrolandığı gözleminden hareket ettiğinizde nasıl bir mekanizma bilgisine ulaşırsınız.

15.49 The evidence indicates that the mechanistic step in which the C–H bond is broken is *not* rate determining. (In the case cited, it makes no difference kinetically if a C–H or C–D bond is broken in electrophilic aromatic substitution.) This evidence is consistent with the two-step mechanism given in Section 15.2. The step in which the aromatic compound reacts with the electrophile (NO_2^+) is the slow rate-determining step. Proton (or deuteron) loss from the arenium ion to return to an aromatic system is a rapid step and has no effect on the overall rate.

15.50 Benzil bromür veya allil bromürden başlayarak aşağıdaki bileşiklerin her birini nasıl sentezleyeceğinizi gösteriniz.

(a) $C_6H_5CH_2CN$	**(d)** $C_6H_5CH_2I$
(b) $C_6H_5CH_2OCH_3$	**(e)** $CH_2{=}CHCH_2N_3$
(c) $C_6H_5CH_2O_2CCH_3$	**(f)** $CH_2{=}CHCH_2OCH_2OCH_2CH(CH_3)_2$

15.50 (a) $$C_6H_5CH_2Br \xrightarrow[\substack{\text{DMF} \\ (\text{-NaBr})}]{\text{NaCN}} C_6H_5CH_2CN$$

(b) $$C_6H_5CH_2Br \xrightarrow[\substack{CH_3OH \\ (\text{-NaBr})}]{CH_3ONa} C_6H_5CH_2OCH_3$$

(c) $$C_6H_5CH_2Br \xrightarrow[\substack{CH_3CO_2H \\ (\text{-NaBr})}]{CH_3CO_2Na} C_6H_5CH_2O_2CCH_3$$

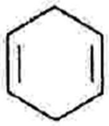
(d) $$C_6H_5CH_2Br \xrightarrow[\substack{\text{acetone} \\ (\text{-NaBr})}]{\text{NaI}} C_6H_5CH_2I$$

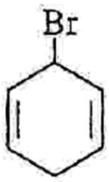
(e) $$CH_2{=}CHCH_2Br \xrightarrow[\substack{\text{acetone} \\ (\text{-NaBr})}]{NaN_3} CH_2{=}CHCH_2N_3$$

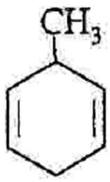
(f) $$CH_2{=}CHCH_2Br \xrightarrow[\substack{(CH_3)_2CHCH_2OH \\ (\text{-NaBr})}]{NaOCH_2CH(CH_3)_2} CH_2{=}CHCH_2OCH_2CH(CH_3)_2$$

15.51 **A**, **B** ve **C** Bileşiklerinin yapılarını bulunuz?

$$\text{Benzen} \xrightarrow[\text{sıvı } NH_3,\ EtOH]{Na} \mathbf{A}\ (C_6H_8) \xrightarrow[CCl_4]{NBS} \mathbf{B}\ (C_6H_7Br) \xrightarrow{(CH_3)_2CuLi} \mathbf{C}\ (C_7H_{10})$$

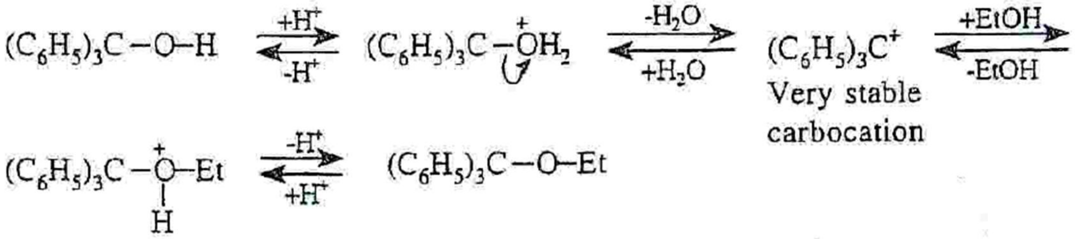
15.51 A = 

B = 

C = 

15.52 1,1,1-Trifeniletanolü eser miktarda kuvvetli asit içeren etanolle ısıttığınızda 1-etoksi-1,1,1-trifenilmetan oluşur. Bu ürünün oluşumunu açıklayan akla yatkın bir mekanizma yazınız?

15.52



$$(C_6H_5)_3C{-}O{-}H \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} (C_6H_5)_3C{-}\overset{+}{O}H_2 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} (C_6H_5)_3C^+ \underset{-EtOH}{\overset{+EtOH}{\rightleftharpoons}}$$

Very stable carbocation

$$(C_6H_5)_3C{-}\underset{H}{\overset{+}{O}}{-}Et \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} (C_6H_5)_3C{-}O{-}Et$$

15.53 **(a)** Bir S_N2 tepkimesinde aşağıdaki halojenürlerin hangisinin en etkin olmasını beklersiniz? **(b)** S_N1 Tepkimesinde hangisi en etkindir? Cevaplarınızı açıklayınız.

$CH_3CH_2CH{=}CHCH_2Br$ $CH_3CH{=}CHCHBrCH_3$ $CH_2{=}CHCBr(CH_3)_2$

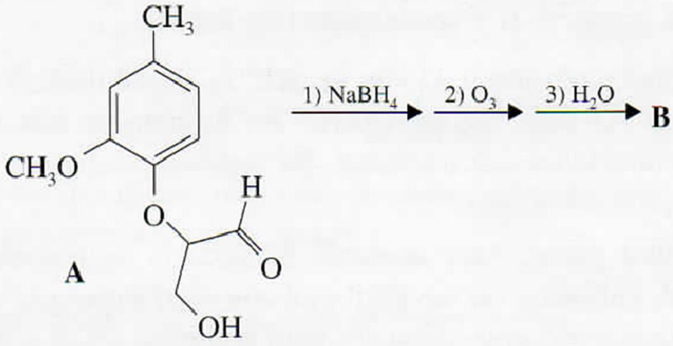
15.53 (a) $CH_3CH_2CH{=}CHCH_2Br$ would be the most reactive in an S_N2 reaction because it is a 1° allylic halide. There would, therefore, be less steric hindrance to the attacking nucleophile.

(b) $CH_2{=}CHCBr(CH_3)_2$ would be the most reactive in an S_N1 reaction because it is a 3° allylic halide. The carbocation formed in the rate-determining step, being both 3° and allylic, would be the most stable.

15.54 Asetanilit aşağıdaki sırada bir seri tepkimeye sokulmuştur. **(a)** der. H_2SO_4; **(b)** HNO_3, ısı; **(c)** H_2O, H_2SO_4, ısı sonra OH^-. Son ürünün ^{13}C NMR spektrumu altı sinyal verir. Son ürünün yapısını yazınız.

15.54 The final product is *o*-nitroaniline. (The reactions are g Section 15.14.) The presence of six signals in the ^{13}C NMR spectrum confirms that the substitution in the final product is *ortho* and not *para*. A final product with para substitution (i.e., *p*-nitroaniline) would have given only four signals in the ^{13}C NMR spectrum.

***15.55** Ligninler doğal bileşiklerle selüloz liflerinin bağlandığı pek çok tipteki kerestenin esas bileşenleri olan makromoleküllerdir. Ligninler değişik küçük moleküllerden (pek çoğunda fenilpropan iskeleti olan) oluşur. Bu öncü moleküller değişik şekillerde kovalent bağlarla bağlanmış olarak bulunurlar ve karmaşık olan ligninleri oluştururlar. Lignin ozonlandığında birçok ürün elde edilir. Bu bileşiklerden biri olan **B** bileşiğinin oluşumunu açıklamak için **A**, lignin bileşiği modeli olarak alınarak aşağıdaki tepkimelere maruz bırakılmıştır. **B** nin yapısı nasıl olabilir?

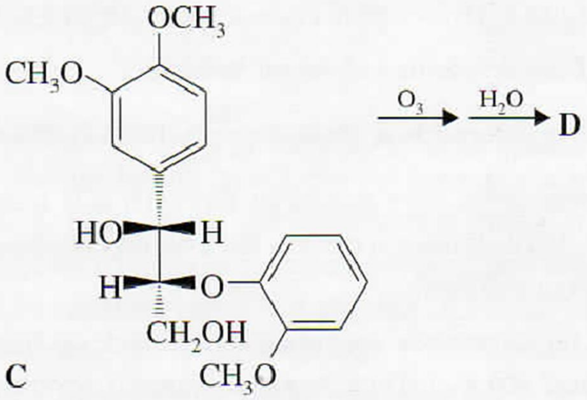


Gaz kromolografi–kütle spektroskopisi (GC/MS) için **B**'yi yeteri kadar uçucu yapmak amacıyla (Altbölüm 9.17) **B** önce, M$^{+\cdot}$ 308 m/z olan tris(*O*-trimetilsilil) türevine dönüştürülür ["Tris", belirtilen kompleks grubun (örneğin, burada trimetilsilil grupları) üç tane olduğu anlamına gelir. İtalik büyük *O* bunların esas bileşiğin oksijen atomlarına bağlandığı ve hidrojen atomlarının yerini aldığı anlamındadır. Benzer şekilde ön ek "bis" iki kompleks grubun varlığını belirtir ve "tetrakis" (aşağıdaki soruda kullanılmıştır) dört anlamına gelir.] B'nin İR spektrumu 3400 cm^{-1} de geniş bir soğurma bandı; ^{1}H NMR spektrumu δ 3,6 da bir tek çoklu pik verir.

B'nin yapısı nedir?

***15.55** $CH_2OHCHOHCH_2OH$ (Glycerol) After sodium borohydride reduction of the aldehyde, ozonolysis oxidatively degrades the aromatic ring, leaving only the polyhydroxy side chain. Water is an alternative to HOAc sometimes used to work up ozonolysis reactions.

***15.56** Ligninde çok, sık rastlanan birim olan **C** bileşiği model olarak kullanıldığında, C ozonlanırsa **D** elde edilir. Değişik yollarla, böyle bir lignin biriminin üç karbon yan zincirinin stereokimyasının, böyle bir yükseltgenme esnasında tamamen değişmeden kaldığı tespit edilmiştir.

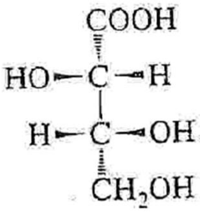


C

GC/MS'de, **D** $M^{+\cdot}$'sı 424 m/z olan tetrakis(*O*-trimetilsilil) türevine dönüştürülmüştür. **D**'nin İR spektrumu 3000 cm^{-1}'de (geniş, kuvvetli) ve 1710 cm^{-1}'de (kuvvetli) bandlar içerir. **D**'nin ^1H NMR spektrumu, D_2O ile etkileştirildikten sonra, δ 3,7 de (çoklu 3H) ve δ 4,2 de (ikili, 1H) içermektedir. DEPT ^{13}C NMR spektrumları δ 64 (CH_2), δ 75 (CH), δ 82 (CH) ve δ 177'de (C) sinyaller vermiştir.

D'nin yapısını stereokimyasıyla birlikte bulunuz?

*15.56



(Threonic acid)

Ozonolysis oxidatively degrades the aromatic rings, leaving only the carboxyl carbon as a remnant of the alkyl substituted benzene ring. Water is an alternative to HOAc used to work up the ozonolysis reaction.

Aldehitler ve Ketonlar I.
Karbonil Grubuna Nükleofilik Katılma

Problem 16.1

(a) $C_5H_{10}O$ Formülüne sahip yedi izomerik aldehit ve ketonun IUPAC türetme adlarını yazınız. (b) C_8H_8O formülüne sahip ve bir benzen halkası içeren tüm aldehit ve ketonların yapılarını ve adlarını (yaygın ve IUPAC türetme adlarını) yazınız.